JOURNAL OF RESEARCH of the National Bureau of Standards
Volume 82, No. 3, November-December 1977

# Phase Equilibria and Crystal Chemistry of Rubidium Niobates and Rubidium Tantalates*

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**(August 2, 1977)**

The phase equilibria relations and crystal chemistry of portions of the $Rb_2O$-$Nb_2O_5$ and $Rb_2O$-$Ta_2O_5$ systems were investigated for structures potentially useful as ionic conductors. A hexagonal tungsten bronze-type (HTB) structure was found in both systems as well as three hexagonal phases with mixed HTB-pyrochlore type structures. Ion exchange experiments between various alkali ions are described for several phases. Unit cell dimensions and x-ray diffraction powder patterns are reported.

Key words: Crystal chemistry; ionic conductivity; non-stoichiometry; phase equilibria; rubidium niobate; rubidium tantalate.

## 1. Introduction

Research in this laboratory in the alkali niobate and tantalate systems has been conducted for the purpose of determining the phase equilibria diagrams of these systems and to observe if structures were present which might be favorable as ionic conductors [1, 2].[1] In this paper the results of the study of portions of the $Rb_2O$-$Nb_2O_5$ and $Rb_2O$-$Ta_2O_5$ systems will be presented. Discussion of the remaining alkali niobate and alkali tantalate systems will be published later.

The phase equilibria relations in the $Rb_2O$-$Nb_2O_5$ system were first studied by Riesman and Holtzberg [3]. On the basis of unindexed x-ray diffraction patterns and density determinations, the compositions of 8 observed phases were reported. These have the molar ratios, $Rb_2O$:$Nb_2O_5$, of 2:15 (11.75 mol per cent $Rb_2O$), 1:4, 4:11 (26.67 mol per cent $Rb_2O$), 1:2, 2:3, 1:1, 4:3 (57.14 mol per cent $Rb_2O$), and 4:1.

Iyer and Smith [4] reported the preparation of phases suggested to have the molar ratios, $Rb_2O$:$Nb_2O_5$, 2:3, 1:2, 1:3 (Riesman and Holtzberg's 4:11), 1:4, and 1:13 (Riesman and Holtzberg's 2:15). In the $Ta_2O_5$ rich portion of the $Rb_2O$-$Ta_2O_5$ system the only compound that was found by Iyer and Smith [4] was $RbTa_3O_8$. Gatehouse et al. [5] reported the unit cell dimensions and partial structure determinations of two of the niobate phases. One of these, "$RbNb_3O_9$", was reported to have a hexagonal tungsten bronze-type (HTB) structure and the other, "$Rb_3Nb_{54}O_{146}$", had a new tetragonal structure with 7-sided tunnels called, in this paper, a Gatehouse tetragonal-bronze (GTB).

## 2. Methods and Results

### 2.1. The System $Rb_2O$:$Nb_2O_5$

The system $Rb_2O$:$Nb_2O_5$ was investigated from the region of 73.33 to 100 mol per cent $Nb_2O_5$. Ten compositions were prepared by dry mixing $Rb_2CO_3$ and $Nb_2O_5$ and calcining in open Pt crucibles at 500 °C for 120 hours and 600 °C for 90 hours with intermediate grindings. Portions from each composition were heated at higher temperatures in sealed Pt tubes in resistance wound quench-type furnaces and quenched into water. Temperature was measured with a 100 Pt/90 Pt-10 Rh thermocouple calibrated against the melting points of gold and palladium, 1064 and 1554 °C, respectively [6]. The temperatures reported are considered to be accurate ±5 °C, up to 1500 °C. Samples were identified at room temperature by x-ray powder diffraction using Ni-filtered Cu radiation and a 1/4° $2\theta$/min scanning rate. X-ray diffraction powder patterns of the quenched specimens were used to establish the phase equilibrium diagram shown in figure 1.

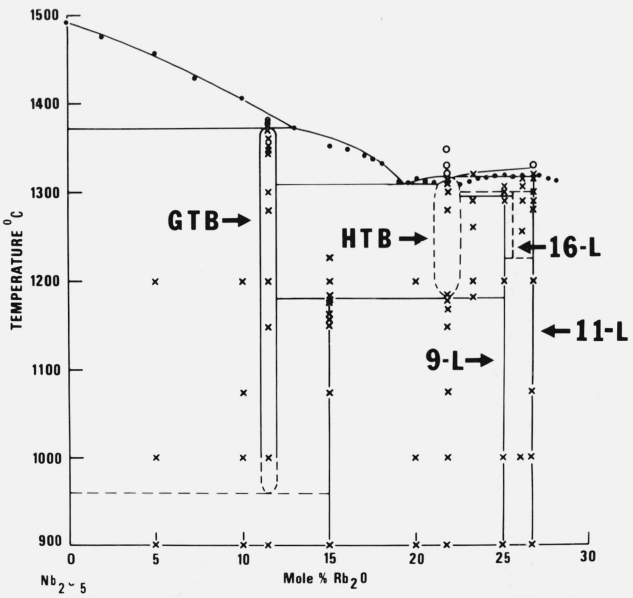


FIGURE 1. *Phase diagram for the system* $Nb_2O_5$:$4Rb_2O$:$11Nb_2O_5$.

* This research was partially supported by NASA-Lewis Research Center Contract C-50821-C.
[1] Figures in brackets indicate the literature references at the end of this paper.

Table 1 details the experimental data for this system. Only the x-ray diffraction pattern of the phase occurring at low temperature at about 15 mol per cent $Rb_2O$ has not been indexed. No single crystals of this phase were obtained.

Table 1. Experimental Data for the System $Nb_2O_5$-$4Rb_2O$:$11Nb_2O_5$.

| Composition | Previous Heat Treatment Temp. °C | Previous Heat Treatment Time hr | Final Heat Treatment[a] Temp. °C | Final Heat Treatment[a] Time hr | Results of Physical Observation | Results of X-ray Diffraction Analysis |
|---|---|---|---|---|---|---|
| $5Rb_2O$:$95Nb_2O_5$ | | | 500 | 120[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | H-$Nb_2O_5$ + 3:17 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 66 | | H-$Nb_2O_5$ + 3:17 |
| | | | 900 | 40 | | H-$Nb_2O_5$ + 3:17 |
| | | | 1000 | 80 | | H-$Nb_2O_5$ + 3:17 |
| | | | 1000 | 111[c] | | |
| | | | 1200 | 88 | | H-$Nb_2O_5$ + GTB |
| $10Rb_2O$:$90Nb_2O_5$ | | | 500 | 120[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 60 | | 3:17 + H-$Nb_2O_5$ |
| | | | 900 | 40 | | 3:17 + H-$Nb_2O_5$ |
| | | | 1000 | 80 | | 3:17 + GTB + H-$Nb_2O_5$ |
| | | | 1000 | 111[c] | | GTB + 3:17 + H-$Nb_2O_5$ |
| | | | 1075 | 60 | | GTB + H-$Nb_2O_5$ |
| | | | 1200 | 88 | | GTB + H-$Nb_2O_5$ |
| $11.5Rb_2O$:$88.5Nb_2O_5$ | | | 500 | 120[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 60 | | 3:17 + H-$Nb_2O_5$ |
| | | | 900 | 40 | | 3:17 + H-$Nb_2O_5$ |
| | | | 1000 | 80 | | GTB + 3:17 |
| | | | 1000 | 111[c] | | GTB + 3:17 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | 1000 | 111 | | | | |
| | | | 1148 | 16 | | GTB |
| | | | 1200 | 88 | | GTB |
| | | | 1280 | 40 | | GTB |
| | | | 1340 | 1.5 | Not melted | |
| | | | 1349 | 23 | | GTB |
| | | | 1352 | .25 | Not melted | |
| | | | 1355 | .33 | Not melted | |
| | | | 1361 | 1 | Not melted | |
| | | | 1369 | .5 | Not melted | |
| | | | 1375 | 1.5 | Partial melted | GTB |
| | | | 1380 | 2 | Completed melted | |
| $15Rb_2O$:$85Nb_2O_5$ | | | 500 | 120[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 750 | 16[c] | | 11-L + H-$Nb_2O_5$ |
| | | | 750 | 16[d] | | 3:17 |
| | | | 800 | 66 | | 3:17 |
| | | | 900 | 40 | | 3:17 |
| | | | 1000 | 80 | | 3:17 |
| | | | 1000 | 111[c] | | 3:17 |
| | | | 1075 | 60 | | 3:17 |
| | | | 1200 | 88 | | GTB + HTB |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | 1000 | 111 | | | | |
| | | | 1156 | 16.5 | | 3:17 |
| | | | 1177 | 24 | | 3:17 + GTB |
| | | | 1180 | 23 | | 3:17 + GTB |
| | | | 1183 | 64 | | HTB + GTB |
| | | | 1226 | 18 | | HTB + GTB |
| | | | 1262 | 18 | | -- |
| | | | 1349 | 23 | | HTB + GTB |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | 1000 | 111 | | | | |
| | 1200 | 16.5 | | | | |
| | | | 1153 | 84[b] | | GTB + 3:17 |
| | | | 1153 | 84[b] | | GTB + 3:17 |
| $20Rb_2O$:$80Nb_2O_5$ | | | 500 | 120[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 66 | | 3:17 + 11-L |
| | | | 900 | 40 | | 3:17 + 11-L |
| | | | 1000 | 80 | | 3:17 + 11-L |
| | | | 1000 | 111[c] | | |
| | | | 1200 | 88 | | 9L + GTB + HTB |
| $21.75Rb_2O$:$78.25Nb_2O_5$ | | | 500 | 120[b] | | |
| | 500 | 120 | 600 | 90[b] | | |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 66 | | 3:17 + 11-L |
| | | | 900 | 40 | | -- |
| | | | 1000 | 80 | | 3:17 + 9-L + 11-L |
| | | | 1000 | 111[c] | | -- |
| | | | 1075 | 60 | | 3:17 + 9-L |
| | | | 1200 | 88 | | 9-L + GTB |
| | | | 1241 | 18 | | HTB + 9-L |
| | | | 1250 | 16 | | HTB + 9-L |
| | | | 1280 | ? | | HTB + 9-L |
| | | | 1300 | 16.5 | | HTB + 11-L + 16-L |

Table 1. Experimental Data for the System $Nb_2O_5$-$4Rb_2O$:$11Nb_2O_5$. (cont.)

| | | | | | | |
|---|---|---|---|---|---|---|
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | 1000 | 111 | | | | |
| | | | 1149 | 23 | | 9-L + 3:17 |
| | | | 1169 | 18 | | 9-L + 3:17 |
| | | | 1181 | 89 | | 9-L + GTB |
| | | | 1184 | 3.5 | | HTB + 9-L |
| | | | 1313 | 64 | | HTB + 11-L |
| | | | 1315 | 0.5 | Not melted | |
| | | | 1320 | 0.5 | Partially melted | HTB + 11-L |
| | | | 1320 | 22 | Completely melted | HTB + 11-L |
| | | | 1328 | 1.5 | Completely melted | |
| | | | 1347 | 16.5 | Completely melted | |
| $23.19Rb_2O:76.81Nb_2O_5$ | | | | | | |
| | 1000 | 63[c] | | | | |
| | | | 1200 | 21[c] | | 9-L + HTB |
| | | | 1255 | 18 | | 9-L + HTB |
| | | | 1290 | 18.5 | | 9-L + HTB |
| | | | 1306 | 22 | | HTB + 11-L |
| $25Rb_2O:75Nb_2O_5$ | | | 500 | 120[b] | | $Nb_2O_3$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | $Nb_2O_3$ + 2:3 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 66 | | 11-L + 3:17 |
| | | | 900 | 40 | | |
| | | | 1000 | 80 | | 11-L + 9-L |
| | | | 1000 | 111[c] | | |
| | | | 1200 | 88 | | 9-L |
| | | | 1280 | ? | | 9-L + HTB |
| | | | 1300 | 40 | | 9-L |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | 1000 | 111 | | | | |
| | | | 1290 | 18.5 | | -- |
| | | | 1300 | 16.5 | | 11-L + HTB |
| $25.5Rb_2O:74.5Nb_2O_5$ | | | 500 | 63[b] | | |
| | 500 | 63 | 600 | 24[b] | | |
| | 500 | 63 | | | | |
| | 600 | 24 | | | | |
| | | | 1000 | 69[c] | | 9-L + 11-L |
| | | | 1249 | 22 | | 9-L |
| | | | 1258 | 67 | | 9-L + 16-L |
| | | | 1262 | 16 | | 9-L + 16-L |
| | | | 1265 | 17 | | 9-L + 16-L |
| | | | 1275 | 117 | | 16-L + ?tr |
| | | | 1284 | 41 | | 16-L + ?tr |
| | | | 1285 | 18 | | 16-L + 11-L |
| | | | 1287 | 67 | | 16-L + 11-L |
| | | | 1291 | 21 | | 16-L + 11-L |
| | | | 1294 | 16 | | 16-L + 11-L |
| | | | 1297 | 22 | | 16-L + 11-L |
| $26.67Rb_2O:73.33Nb_2O_5$ | | | 500 | 120[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 90[b] | | H-$Nb_2O_5$ + 2:3 |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 750 | 60 | | 11-L |
| | | | 800 | 66 | | 11-L |
| | | | 900 | 40 | | 11-L |
| | | | 1000 | 80 | | 11-L |
| | | | 1000 | 111[c] | | 11-L |
| | | | 1075 | 60 | | 11-L |
| | | | 1200 | 88 | | 11-L |
| | | | 1241 | 18 | | 11-L |
| | | | 1280 | 40 | | 11-L |
| | | | 1300 | 40 | | H-L |
| | 500 | 120 | | | | |
| | 500 | 90 | | | | |
| | 1000 | 111 | | | | |
| | | | 1290 | 18.5 | | 11-L |
| | | | 1306 | 22 | | 11-L |
| | | | 1316 | 0.5 | Not melted | |
| | | | 1316 | 16 | Partially melted | |
| | | | 1320 | 0.5 | Partially melted | |
| | | | 1330 | 1.5 | Completely melted | |

[a] Except as indicated by a footnote the samples were quenched into water from the temperature indicated.

[b] The samples were calcined in open Pt crucibles and pulled from the furnaces at the temperatures indicated. $Rb_2O$ may have been volatilized during these calcines thereby changing the composition to one greater in mole percent $Nb_2O_5$.

[c] The sample was in a large sealed Pt tube and pulled from the furnace at the temperature and cooled rapidly on a chill block.

[d] The sample was removed from the furnace at the temperature indicated and immediately dunked into a beaker of water.

This phase can be identified by its major diffraction peaks occurring at $d$ = 6.92, 3.97, 3.92, 3.54, 3.44, 3.27, 3.16, 2.779, and 2.472 A. X-ray powder diffraction patterns of all other phases are given in tables 2–6. Intensities listed in tables 2–6 are given relative to the strongest peak height above background. The phases were found to have the structures (in order of increasing alkali content) of the Gatehouse tetragonal bronze-type (GTB), an orthorhombic distortion of the hexagonal tungsten bronze-type (HTB), and three hexagonal phases with $c$ axes approximately 3.9 A × 9, × 16, and × 11 which were called "9-layer", "16-layer", and "11-layer" phases in the $K_2O$-$Ta_2O_5$ system [1, 7].

Table 2

X-ray Diffraction Powder Pattern of the "Gatehouse-Tetragonal-Bronze"-Like Phase Occurring at the Composition 11.5$Rb_2O$:88.5$Nb_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 19.53 | 110 | 4.52 | 4.54 | 5 |
| 13.82 | 200 | 6.39 | 6.43 | 7 |
| 12.34 | 210 | 7.16 | 7.19 | 6 |
| 9.72 | 220 | 9.09 | 9.09 | 8 |
| 8.71 | 310 | 10.15 | 10.17 | 8 |
| 7.64 | 320 | 11.58 | 11.60 | 9 |
| 6.67 | 410 | 13.27 | 13.27 | 6 |
| 3.964 | 001 | 22.41 | 22.40 | 100 |
| 3.886 | 111 | 22.87 | 22.87 | 11 |
| 3.811 | 640 | 23.32 | 23.32 | 6 |
| 3.672 | 221 | 24.22 | 24.22 | 5 |
| 3.610 | 730 | 24.64 | 24.65 | 28 |
| 3.520 | 650 | 25.28 | 25.29 | 19 |
| 3.435 | 800 | 25.92 | 25.91 | 28 |
| 3.409 | 740 | 26.12 | 26.12 | 32 |
| 3.333 | 820/421 | 26.72 | 26.73/26.73 | 41 |
| 3.238 | 660 | 27.52 | 27.52 | 52 |
| 3.217 | 830/431 | 27.71 | 27.71/27.72 | 55 |
| 3.194 | 750/511 | 27.91 | 27.90/27.91 | 8 |
| 3.131 | 521 | 28.48 | 28.48 | 4 |
| 3.071 | 840/441 | 29.05 | 29.04/29.04 | 7 |
| 3.033 | 910 | 29.42 | 29.41 | 22 |
| 2.980 | 760 | 29.96 | 29.95 | 36 |
| 2.914 | 850 | 30.66 | 30.66 | 25 |
| 2.790 | 940/701 | 32.05 | 32.05/32.05 | 8 |
| 2.778 | 770 | 32.20 | 32.22 | 8 |
| 2.748 | 10,0,0/860 | 32.56 | 32.55/32.56 | 10 |
| 2.735 | 10,1,0/721 | 32.72 | 32.72/32.72 | 7 |
| 2.669 | 950/731 | 33.55 | 33.54/33.55 | 9 |
| 2.632 | 10,3,0/651 | 34.03 | 34.04/34.03 | 6 |
| 2.597 | 801 | 34.51 | 34.51 | 9 |
| 2.585 | 870/741 | 34.67 | 34.67/34.67 | 9 |
| 2.552 | 10,4,0/821 | 35.14 | 35.14/35.14 | 15 |
| 2.510 | 661 | 35.74 | 35.76 | 9 |
| 2.500 | 11,0,0/831 | 35.89 | 35.91/35.92 | 9 |
| 2.4886 | 11,1,0/751 | 36.06 | 36.07/36.07 | 5 |
| 2.4199 | 901 | 37.12 | 37.13 | 3 |
| 2.4087 | 970/911 | 37.30 | 37.27/37.28 | 6 |
| 2.3822 | 761 | 37.73 | 37.72 | 7 |
| 2.3474 | 11,4,0/851 | 38.31 | 38.30/38.31 | 10 |
| 2.2822 | 980/941 | 39.45 | 39.45/39.45 | 6 |
| 2.2586 | 12,2,0/10,0,1 | 39.88 | 39.87/39.88 | 6 |
| 2.1726 | 12,4,0 | 41.53 | 41.53 | 6 |
| 2.1661 | 871 | 41.66 | 41.67 | 3 |
| 2.1592 | 990 | 41.80 | 41.80 | 3 |
| 2.1077 | 11,7,0/11,1,1 | 42.87 | 42.87/42.87 | 4 |
| 2.0887 | 13,2,0/10,5,1 | 43.28 | 43.26/43.27 | 4 |
| 1.9836 | 12,0,1/002 | 45.70 | 45.71/45.72 | 26 |
| 1.9628 | 14,0,0/12,2,1/202 | 46.21 | 46.20/46.21/46.22 | 4 |
| 1.9434 | 10,10,0/222 | 46.70 | 46.70/46.72 | 5 |
| 1.9383 | 12,3,1/302 | 46.83 | 46.83/46.84 | 4 |
| 1.9328 | 312 | 46.97 | 46.96 | 5 |
| 1.9194 | 11,6,1/322 | 47.32 | 47.32/47.33 | 9 |
| 1.9053 | 12,8,0/12,4,1/402 | 47.69 | 47.68/47.69/47.70 | 7 |
| 1.9005 | 412 | 47.82 | 47.82 | 5 |
| 1.8867 | 14,4,0/10,8,1/422 | 48.19 | 48.17/48.17/48.18 | 13 |
| 1.8482 | 11,10,0/13,2,1/522 | 49.26 | 49.25/49.25/49.26 | 14 |
| 1.8267 | 532 | 49.88 | 49.85 | 7 |
| 1.8030 | 622 | 50.58 | 50.56 | 7 |
| 1.7997 | 13,8,0/11,8,1/542 | 50.68 | 50.66/50.66/50.67 | 10 |
| 1.7666 | 11,11,0/13,5,1/552 | 51.70 | 51.70/51.70/51.71 | 5 |
| 1.7375 | 13,9,0/11,9,1/732 | 52.63 | 52.61/52.61/52.62 | 9 |
| 1.7140 | 742 | 53.41 | 53.41 | 4 |
| 1.7039 | 14,8,0/14,4,1/822 | 53.75 | 53.73/53.74/53.75 | 10 |
| 1.6911 | 662 | 54.19 | 54.19 | 6 |
| 1.6874 | 12,11,0/832 | 54.32 | 54.29/54.30 | 8 |
| 1.6752 | 13,10,0/11,10,1 | 54.75 | 54.73/54.74 | 6 |
| 1.6659 | 14,4,0/842 | 55.08 | 55.06/55.08 | 3 |
| 1.6631 | 12,9,1/902 | 55.18 | 55.18/55.19 | 3 |
| 1.6601 | 15,7,0/15,1,1/912 | 55.29 | 55.28/55.29/55.30 | 7 |
| 1.6510 | 14,9,0/15,2,1/762 | 55.62 | 55.61/55.62/55.62 | 4 |
| 1.6393 | 16,5,0/13,8,1/852 | 56.05 | 56.04/56.05/56.06 | 11 |
| 1.6130 | 772 | 57.05 | 57.03 | 4 |
| 1.6090 | 16,6,0/12,10,1/862 | 57.20 | 57.23/57.23/57.24 | 4 |
| 1.5915 | 17,3,0/13,9,1/952 | 57.89 | 57.87/57.87/57.88 | 5 |

[a/] This powder diffraction was obtained from material heated in a sealed Pt tube at 1280°C for 40 hours and quenched into water.

[b/] This diffraction pattern was indexed with the aid of single crystal precession patterns on the basis of a tetragonal unit cell with a=27.484±.003Å and c=3.9656±.0004Å.

Table 3

X-ray Diffraction Pattern of the Hexagonal Bronze-Like Phase From the Composition 21.75$Rb_2O$:78.25$Nb_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 6.53 | 110 | 13.55 | 13.55 | 16 |
| 3.900 | 001 | 22.78 | 22.80 | 25 |
| 3.348 | 111 | 26.60 | 26.61 | 61 |
| 3.262 | 220 | 27.32 | 27.30 | 100 |
| 3.251 | 400 | 27.41 | 27.44 | 85 |
| 2.706 | 311 | 33.07 | 33.09 | 44 |
| 2.501 | 221 | 35.85 | 35.86 | 15 |
| 2.4966 | 401 | 35.94 | 35.96 | 15 |
| 2.0868 | 131 | 43.32 | 43.32 | 6 |
| 2.0810 | 421 | 43.45 | 43.44 | 8 |
| 1.9494 | 002 | 46.55 | 46.56 | 67 |
| 1.8998 | 331 | 47.84 | 47.84 | 14 |
| 1.8926 | 601 | 48.03 | 48.03 | 12 |
| 1.8880 | 040 | 48.16 | 48.17 | 21 |
| 1.8784 | 620 | 48.42 | 48.42 | 40 |
| 1.8077 | 530 | 50.44 | 50.44 | 2 |
| 1.6990 | 041 | 53.92 | 53.93 | 5 |
| 1.6923 | 621 | 54.15 | 54.16 | 11 |
| 1.6737 | 222 | 54.80 | 54.82 | 22 |
| 1.6709 | 402 | 54.90 | 54.89 | 17 |
| 1.6434 | 241 | 55.90 | 55.90 | 5 |
| 1.6396 | 331 | 56.04 | 56.03 | 6 |
| 1.6359 | 711 | 56.18 | 56.18 | 8 |
| 1.6319 | 440 | 56.33 | 56.33 | 17 |
| 1.6239 | 800 | 56.63 | 56.63 | 8 |
| 1.5054 | 441 | 61.55 | 61.56 | 5 |
| 1.4999 | 150 | 61.80 | 61.80 | 4 |
| 1.4002 | 151 | 66.75 | 66.77 | 4 |
| 1.3941 | 731/821 | 67.08 | 67.04/67.13 | 4 |
| 1.3556 | 042 | 69.25 | 69.24 | 6 |
| 1.3525 | 622 | 69.43 | 69.44 | 13 |
| 1.3396 | 351 | 70.20 | 70.23 | 3 |
| 1.3371 | 641 | 70.35 | 70.38 | 4 |
| 1.3325 | 911 | 70.63 | 70.64 | 4 |
| 1.3277 | 242 | 70.92 | 70.95 | 2 |
| 1.2994 | 003/10,0,0 | 72.71 | 72.72/72.73 | 3 |
| 1.2743 | 113 | 74.38 | 74.38 | 2 |
| 1.2508 | 442 | 76.02 | 76.00 | 4 |
| 1.2476 | 802 | 76.25 | 76.26 | 3 |
| 1.2313 | 840 | 77.45 | 77.47 | 2 |
| 1.2283 | 023/10,2,0 | 77.67 | 77.66/77.66 | 4 |

[a/] This powder diffraction pattern was obtained from ground single crystal pulled from a melt of 21.75$Rb_2O$:78.25$Nb_2O_5$ by the Czochralski method.

[b/] This diffraction pattern was indexed with the aid of single crystal precession patterns on the basis of an orthorhombic unit cell with a=12.991±.004Å, b=7.550±.001Å and c=3.8978±.0008Å.

## 2.2. The System $Rb_2O$-$Ta_2O_5$

The system $Rb_2O$-$Ta_2O_5$ was investigated from 73.33 to 100 mol per cent $Ta_2O_5$. Eight compositions were prepared by dry mixing $Rb_2CO_3$ and $Ta_2O_5$, and heating at 500 °C for 120 hours and 600 °C for 110 hours with intermediate grindings. Portions from each composition were heated at higher temperatures in sealed Pt capsules in resistance wound quench-type furnaces and quenched into water.

## Table 4

X-ray Diffraction Powder Pattern of the "9-L" Phase Occurring at the Composition $Rb_2O:3Nb_2O_5$.[a]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b] | $I_{obs}$ |
|---|---|---|---|---|
| 18.16 | 002 | 4.86 | 4.86 | 3 |
| 9.11 | 004 | 9.70 | 9.72 | 100 |
| 6.515 | 100 | 13.58 | 13.59 | 25 |
| 6.058 | 006 | 14.61 | 14.61 | 15 |
| 5.378 | 103 | 15.43 | 15.44 | 6 |
| 4.852 | 105 | 18.27 | 18.28 | 4 |
| 4.564 | 008 | 19.51 | 19.52 | 40 |
| 3.728 | 108 | 23.85 | 23.86 | 7 |
| 3.473 | 114 | 25.63 | 25.62 | 34 |
| 3.433 | 109 | 25.93 | 25.94 | 90 |
| 3.252 | 200 | 27.40 | 27.37 | 34 |
| 3.245 | 201 | 27.46 | 27.49 | 36 |
| 3.195 | 116 | 27.90 | 27.91 | 29 |
| 3.174 | 1,0,10 | 28.09 | 28.09 | 8 |
| 3.142 | 203 | 28.38 | 28.37 | 49 |
| 3.064 | 204 | 29.12 | 29.11 | 13 |
| 3.027 | 0,0,12 | 29.48 | 29.46 | 68 |
| 2.969 | 205 | 30.07 | 30.05 | 44 |
| 2.896 | 118 | 30.85 | 30.85 | 38 |
| 2.868 | 206 | 31.16 | 31.16 | 4 |
| 2.758 | 207 | 32.44 | 32.43 | 7 |
| 2.732 | 1,0,12 | 32.57 | 32.57 | 14 |
| 2.646 | 208 | 33.85 | 33.88 | 14 |
| 2.613 | 1,1,10 | 34.29 | 34.29 | 7 |
| 2.597 | 0,0,14 | 34.51 | 34.51 | 7 |
| 2.535 | 209 | 35.38 | 35.38 | 16 |
| 2.4602 | 210 | 36.49 | 36.48 | 3 |
| 2.4557 | 211 | 36.56 | 36.57 | 4 |
| 2.4124 | 1,0,14/213 | 37.24 | 37.25/37.25 | 5 |
| 2.3581 | 1,1,12 | 38.13 | 38.12 | 10 |
| 2.2181 | 2,0,12 | 40.64 | 40.65 | 3 |
| 2.1696 | 2,0,13 | 42.59 | 42.59 | 6 |
| 2.1110 | 304 | 42.80 | 42.80 | 12 |
| 2.1026 | 219 | 42.98 | 43.00 | 11 |
| 2.0800 | 305 | 43.47 | 43.48 | 6 |
| 2.0429 | 306 | 44.30 | 44.30 | 10 |
| 2.0321 | 1,0,17 | 44.55 | 44.56 | 8 |
| 2.0200 | 0,0,18 | 44.83 | 44.84 | 65 |
| 1.9580 | 308 | 46.33 | 46.32 | 17 |
| 1.9438 | 2,0,15 | 46.69 | 46.69 | 12 |
| 1.9102 | 2,1,12 | 47.56 | 47.57 | 9 |
| 1.8790 | 220 | 48.40 | 48.39 | 41 |
| 1.8631 | 3,0,10/2,0,16 | 48.84 | 48.83/48.84 | 5 |
| 1.8409 | 224 | 49.47 | 49.48 | 5 |
| 1.8356 | 1,0,19 | 49.62 | 49.62 | 4 |
| 1.8054 | 310 | 50.51 | 50.50 | 4 |
| 1.7872 | 2,0,17 | 51.06 | 51.06 | 20 |
| 1.7647 | 3,0,12 | 51.76 | 51.78 | 5 |
| 1.7164 | 2,0,18 | 53.33 | 53.34 | 18 |
| 1.6726 | 1,0,21 | 54.84 | 54.83 | 6 |
| 1.6524 | 0,0,22 | 55.57 | 55.57 | 6 |
| 1.6488 | 319 | 55.70 | 55.71 | 12 |
| 1.6364 | 1,1,20 | 56.16 | 56.16 | 4 |
| 1.6271 | 400 | 56.51 | 56.49 | 5 |
| 1.6135 | 403 | 57.03 | 57.04 | 12 |
| 1.6019 | 404/1,0,22 | 57.48 | 57.47/57.49 | 5 |
| 1.5971 | 2,2,12 | 57.67 | 57.67 | 12 |
| 1.5888 | 405 | 58.00 | 58.02 | 5 |
| 1.5693 | 3,0,16 | 58.79 | 58.79 | 5 |
| 1.5513 | 3,1,12 | 59.54 | 59.55 | 5 |
| 1.5329 | 408 | 60.33 | 60.36 | 5 |
| 1.5281 | 2,0,21 | 60.54 | 60.53 | 24 |
| 1.5226 | 2,2,14 | 60.78 | 60.79 | 11 |
| 1.5149 | 0,0,24 | 61.12 | 61.13 | 4 |
| 1.5098 | 409 | 61.35 | 61.36 | 7 |
| 1.4934 | 320 | 62.10 | 62.09 | 2 |
| 1.4826 | 3,1,14/323 | 62.60 | 62.61/62.61 | 4 |
| 1.4786 | 3,0,18 | 62.79 | 62.80 | 5 |
| 1.4627 | 325 | 63.55 | 63.54 | 2 |
| 1.4338 | 4,0,12 | 64.99 | 64.99 | 2 |
| 1.4215 | 2,0,23 | 65.62 | 65.61 | 7 |
| 1.4187 | 328 | 65.77 | 65.76 | 5 |
| 1.4038 | 414 | 66.56 | 66.56 | 5 |
| 1.4004 | 329 | 66.74 | 66.71 | 8 |
| 1.3980 | 0,0,26 | 66.87 | 66.86 | 11 |
| 1.3793 | 3,1,17 | 67.90 | 67.88 | 4 |
| 1.3759 | 2,2,18 | 68.09 | 68.09 | 17 |
| 1.3557 | 418 | 69.25 | 69.23 | 5 |
| 1.3188 | 1,0,27 | 71.48 | 71.50 | 5 |
| 1.3024 | 500 | 72.52 | 72.54 | 3 |
| 1.2950 | 3,2,14/503 | 73.00 | 73.02/73.03 | 7 |
| 1.2674 | 4,0,18 | 74.86 | 74.86 | 7 |
| 1.2411 | 334/2,2,22 | 76.73 | 76.72/76.74 | 3 |
| 1.2299 | 421 | 77.56 | 77.57 | 2 |
| 1.2243 | 423 | 77.98 | 77.99 | 6 |
| 1.2158 | 2,1,26 | 78.63 | 78.64 | 2 |
| 1.2131 | 425 | 78.84 | 78.83 | 5 |
| 1.1858 | 4,0,21 | 81.02 | 81.02 | 6 |
| 1.1696 | 510 | 82.39 | 82.41 | 3 |
| 1.1530 | 4,2,11 | 83.84 | 83.83 | 5 |
| 1.1353 | 2,0,30 | 85.43 | 85.42 | 3 |
| 1.1216 | 2,2,26 | 86.75 | 86.73 | 7 |
| 1.0894 | 600 | 90.47 | 90.46 | 5 |
| 1.0792 | 3,1,27 | 91.09 | 91.06 | 2 |
| 1.0662 | 514/433 | 92.52 | 92.52/92.52 | 3 |
| 1.0582 | 3,0,30 | 93.43 | 93.45 | 2 |
| 1.0505 | 4,2,18 | 94.32 | 94.29 | 3 |

[a] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1200°C for 88 hours and quenched into water.

[b] This diffraction pattern was indexed on the basis of a hexagonal unit cell with a=7.5179±.0002Å and c=36.353±.001Å by comparison with single crystal patterns of an apparently isostructural phase in the $K_2O:Ta_2O_5$ system.

## Table 5

X-ray Diffraction Powder Pattern of the "16-L" Phase Occurring at the Composition $25.5Rb_2O:74.5Nb_2O_5$.[a]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b] | $I_{obs}$ |
|---|---|---|---|---|
| 16.35 | 004 | 5.40 | 5.42 | 5 |
| 10.89 | 006 | 8.11 | 8.14 | 14 |
| 8.16 | 008 | 10.83 | 10.86 | 23 |
| 6.51 | 0,0,10/100 | 13.59 | 13.59/13.60 | 33 |
| 6.49 | 101 | 13.64 | 13.66 | 40 |
| 6.34 | 103 | 14.19 | 14.20 | 5 |
| 6.05 | 104 | 14.63 | 14.65 | 5 |
| 5.82 | 105 | 15.21 | 15.21 | 7 |
| 5.58 | 106 | 15.86 | 15.87 | 11 |
| 4.655 | 0,0,14 | 19.06 | 19.07 | 21 |
| 4.377 | 1,0,11 | 20.27 | 20.26 | 7 |
| 3.757 | 110 | 23.66 | 23.66 | 7 |
| 3.661 | 114 | 24.29 | 24.29 | 6 |
| 3.550 | 116 | 25.06 | 25.06 | 15 |
| 3.449 | 1,0,16 | 25.81 | 25.80 | 79 |
| 3.413 | 118 | 26.09 | 26.10 | 39 |
| 3.301 | 1,0,17 | 26.99 | 26.99 | 20 |
| 3.250 | 1,1,10/200 | 27.42 | 27.39/27.39 | 100 |
| 3.191 | 204 | 27.94 | 27.94 | 21 |
| 3.156 | 205 | 28.25 | 28.25 | 15 |
| 3.115 | 206 | 28.63 | 28.62 | 54 |
| 3.070 | 207 | 29.06 | 29.05 | 20 |
| 3.020 | 208 | 29.55 | 29.54 | 43 |
| 2.968 | 209 | 30.08 | 30.09 | 50 |
| 2.960 | 0,0,22 | 30.17 | 30.17 | 48 |
| 2.922 | 1,1,14 | 30.57 | 30.56 | 43 |
| 2.796 | 1,0,21 | 31.98 | 31.95 | 14 |
| 2.761 | 1,1,16 | 32.40 | 32.41 | 5 |
| 2.712 | 0,0,24 | 33.00 | 32.99 | 7 |
| 2.693 | 1,0,22 | 33.24 | 33.23 | 7 |
| 2.683 | 1,1,17 | 33.37 | 33.38 | 4 |
| 2.667 | 2,0,14 | 33.57 | 33.59 | 7 |
| 2.603 | 0,0,25/2,0,15 | 34.42 | 34.40/34.42 | 13 |
| 2.540 | 2,0,16 | 35.31 | 35.29 | 21 |
| 2.503 | 0,0,26/1,0,24 | 35.85 | 35.83 | 6 |
| 2.4595 | 210 | 36.50 | 36.50 | 6 |
| 2.1111 | 307 | 42.80 | 42.77 | 9 |
| 2.1055 | 2,1,16 | 42.92 | 42.93 | 10 |
| 2.0957 | 308 | 43.13 | 43.13 | 12 |
| 2.0788 | 309 | 43.50 | 43.52 | 8 |
| 2.0581 | 3,0,10 | 43.96 | 43.96 | 20 |
| 2.0342 | 2,1,18 | 44.50 | 44.51 | 39 |
| 1.9766 | 1,1,28 | 45.87 | 45.85 | 6 |
| 1.9658 | 3,0,14 | 46.14 | 46.14 | 10 |
| 1.9267 | 1,1,29/2,1,21 | 47.13 | 47.11/47.13 | 6 |
| 1.8779 | 220/221 | 48.43 | 48.42/48.44 | 48 |
| 1.8304 | 228 | 49.78 | 49.78 | 4 |
| 1.8048 | 2,0,30/3,0,20<br>2,2,10/310 | 50.53 | 50.51/50.52<br>50.53/50.53 | 18 |
| 1.7876 | 2,1,25/315 | 51.05 | 51.03/51.05 | 19 |
| 1.7645 | 2,0,31 | 51.76 | 51.76 | 9 |
| 1.7599 | 0,0,37 | 51.91 | 51.91 | 8 |
| 1.7496 | 3,0,22 | 52.24 | 52.24 | 8 |
| 1.6943 | 3,0,24 | 54.08 | 54.09 | 5 |
| 1.6868 | 2,0,33/2,2,17 | 54.34 | 54.33/54.35 | 6 |
| 1.6587 | 2,1,29 | 55.34 | 55.36 | 4 |
| 1.6570 | 1,0,38 | 55.40 | 55.40 | 4 |
| 1.6500 | 3,1,16 | 55.66 | 55.67 | 11 |
| 1.6329 | 3,1,17 | 56.29 | 56.30 | 4 |
| 1.6279 | 0,0,40 | 56.48 | 56.48 | 8 |
| 1.6261 | 401 | 56.55 | 56.54 | 10 |
| 1.6222 | 403 | 56.70 | 56.70 | 6 |
| 1.6122 | 3,0,27 | 57.08 | 57.06 | 4 |
| 1.6092 | 406 | 57.20 | 57.21 | 11 |
| 1.5956 | 408 | 57.73 | 57.75 | 15 |
| 1.5863 | 3,0,28/2,2,22 | 58.10 | 58.11/58.11 | 10 |
| 1.5594 | 1,1,38 | 59.20 | 59.22 | 4 |
| 1.5480 | 2,0,37 | 59.68 | 59.69 | 4 |
| 1.5442 | 2,2,24 | 59.84 | 59.84 | 7 |
| 1.5356 | 4,0,14 | 60.21 | 60.22 | 4 |
| 1.5233 | 2,2,25/4,0,15 | 60.75 | 60.74/60.75 | 10 |
| 1.5149 | 0,0,43 | 61.12 | 61.15 | 15 |
| 1.5109 | 2,1,34/4,0,16 | 61.30 | 61.30/61.32 | 12 |
| 1.5027 | 2,2,26/3,1,24 | 61.67 | 61.67/61.68 | 9 |
| 1.4927 | 320/321 | 62.13 | 62.13/62.15 | 7 |
| 1.4888 | 323 | 62.31 | 62.29 | 6 |
| 1.4794 | 0,0,44/326 | 62.75 | 62.73/62.78 | 6 |
| 1.4217 | 3,2,14 | 65.61 | 65.63 | 4 |
| 1.4152 | 0,0,46 | 65.95 | 65.94 | 14 |
| 1.4078 | 416 | 66.34 | 66.34 | 4 |
| 1.4044 | 1,1,43 | 66.52 | 66.52 | 5 |
| 1.4009 | 3,2,16 | 66.71 | 66.68 | 10 |
| 1.3801 | 2,2,32/3,2,18 | 67.85 | 67.85/67.86 | 12 |
| 1.3760 | 1,1,44 | 68.08 | 68.03 | 11 |
| 1.3171 | 4,0,29 | 71.58 | 71.57 | 5 |
| 1.3012 | 500/501 | 72.59 | 72.58/72.60 | 14 |

[a] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1275°C for 117 hours and quenched into water.

[b] This pattern was indexed on the basis of a hexagonal unit cell with a=7.5138±.0005Å and c=65.115±.009Å.

Table 6

X-ray Diffraction Pattern of the "11-L" Phase Occurring at the Composition $4Rb_2O:11Nb_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 14.41 | 003 | 6.13 | 6.14 | 8 |
| 7.19 | 006 | 12.30 | 12.29 | 23 |
| 6.44 | 101 | 13.74 | 13.74 | 21 |
| 6.23 | 012 | 14.17 | 14.19 | 4 |
| 5.58 | 104 | 15.86 | 15.88 | 9 |
| 4.792 | 009 | 18.50 | 18.48 | 6 |
| 4.160 | 018 | 21.34 | 21.36 | 4 |
| 3.759 | 110 | 23.65 | 23.64 | 2 |
| 3.639 | 113 | 24.44 | 24.44 | 9 |
| 3.599 | 1,0,10/0,0,12 | 24.72 | 24.72/24.72 | 10 |
| 3.361 | 0,1,11 | 26.48 | 26.49 | 61 |
| 3.334 | 116 | 26.72 | 26.72 | 71 |
| 3.247 | 021 | 27.45 | 27.44 | 22 |
| 3.212 | 202 | 27.65 | 27.67 | 6 |
| 3.117 | 024 | 28.62 | 28.60 | 19 |
| 3.049 | 205 | 29.27 | 29.28 | 100 |
| 2.958 | 1,0,13 | 30.19 | 30.18 | 16 |
| 2.877 | 0,0,15 | 31.06 | 31.04 | 68 |
| 2.789 | 208 | 32.07 | 32.07 | 8 |
| 2.601 | 0,2,10/1,1,12 | 34.45 | 34.46/34.47 | 22 |
| 2.4921 | 1,0,16 | 36.01 | 35.99 | 5 |
| 2.3983 | 0,0,18 | 37.47 | 37.46 | 3 |
| 2.2851 | 1,1,15 | 39.40 | 39.38 | 5 |
| 2.1461 | 1,0,19 | 42.07 | 42.07 | 4 |
| 2.0855 | 1,2,11 | 43.35 | 43.34 | 12 |
| 2.0797 | 306 | 43.48 | 43.50 | 20 |
| 2.0554 | 0,0,21 | 44.02 | 44.00 | 71 |
| 2.0227 | 1,1,18 | 44.77 | 44.77 | 5 |
| 2.0024 | 2,0,17 | 45.25 | 45.23 | 7 |
| 1.9788 | 309 | 45.82 | 45.83 | 8 |
| 1.9240 | 1,2,14 | 47.20 | 47.19 | 4 |
| 1.8817 | 220 | 48.33 | 48.36 | 52 |
| 1.8653 | 223 | 48.78 | 48.80 | 4 |
| 1.8189 | 226 | 50.11 | 50.09 | 12 |
| 1.8034 | 1,1,21/0,1,23 | 50.57 | 50.55/50.55 | 10 |
| 1.7998 | 2,0,20/0,0,24 | 50.68 | 50.69/50.70 | 18 |
| 1.7685 | 315/1,2,17 | 51.64 | 51.64/51.66 | 2 |
| 1.7508 | 229 | 52.20 | 52.20 | 1 |
| 1.6692 | 1,0,25 | 54.96 | 54.95 | 2 |
| 1.6662 | 1,3,10/2,2,12 | 55.07 | 55.05 | 2 |
| 1.6416 | 3,1,11 | 55.97 | 55.98 | 27 |
| 1.6273 | 401 | 56.50 | 56.50 | 1 |
| 1.6234 | 1,2,20/1,1,24 | 56.65 | 56.66/56.67 | 2 |
| 1.6096 | 0,1,26 | 57.18 | 57.20 | 3 |
| 1.6010 | 045 | 57.52 | 57.54 | 12 |
| 1.5989 | 0,0,27 | 57.60 | 57.59 | 7 |
| 1.5873 | 1,3,13 | 58.06 | 58.07 | 1 |
| 1.5745 | 407/2,2,15 | 58.58 | 58.57/58.58 | 18 |
| 1.5594 | 048/3,1,14 | 59.20 | 59.21/59.22 | 3 |
| 1.5343 | 2,1,22 | 60.27 | 60.25 | 2 |
| 1.5249 | 0,2,25/4,0,10 | 60.68 | 60.64/60.73 | 14 |
| 1.5011 | 1,0,28 | 61.75 | 61.77 | 4 |
| 1.4935 | 321 | 62.10 | 62.09 | 6 |
| 1.4793 | 2,0,26 | 62.76 | 62.75 | 8 |
| 1.4387 | 0,0,30 | 64.74 | 64.71 | 12 |
| 1.4142 | 1,3,19/2,1,25 | 66.00 | 66.00/66.01 | 1 |
| 1.3943 | 416/4,0,16 | 67.07 | 67.05/67.07 | 8 |
| 1.3873 | 2,2,21 | 67.45 | 67.43 | 8 |
| 1.3627 | 419/3,2,13 | 68.84 | 68.82/68.83 | 3 |
| 1.3076 | 3,2,16 | 72.18 | 72.20 | 5 |
| 1.2995 | 0,4,20/2,2,24 | 72.70 | 72.66/72.67 | 12 |
| 1.2737 | 1,2,29 | 74.42 | 74.40 | 1 |

[a/] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1306°C for 22 hours and quenched into water.

[b/] This diffraction pattern was indexed with the aid of single crystal precession patterns on the basis of a hexagonal unit cell with a=7.5224±.0007Å and c=43.180±.005Å, h+k+ℓ=3n.

Temperature was measured with a 100 Pt/90 Pt-10 Rh thermocouple calibrated against the melting points of gold and palladium. The temperatures reported are considered to be accurate to ±5 °C up to 1500 °C. Above 1550 °C temperatures were measured with a NBS calibrated optical pyrometer recalibrated against the melting points of palladium and platinum 1554 and 1772 °C [6]. The pyrometer uncertainty is estimated at ±10° to 1700 °C and ±15° at 1750 °C. The variation in structure type with alkali content was similar to that observed in the $Rb_2O$-$Nb_2O_5$ system with the exception of the low temperature unindexed phase. Samples were identified at room temperature by x-ray powder diffraction using Ni-filtered Cu radiation and a 1/4° $2\theta$/min scanning rate. The x-ray diffraction powder patterns derived from quenched specimens were used to construct the phase diagram shown in figure 2 and the experimental results are listed in table 7. X-ray diffraction patterns for all the phases in this subsystem are given in tables 8–11. Intensities listed in tables 8–11 are given relative to the strongest peak height above background.

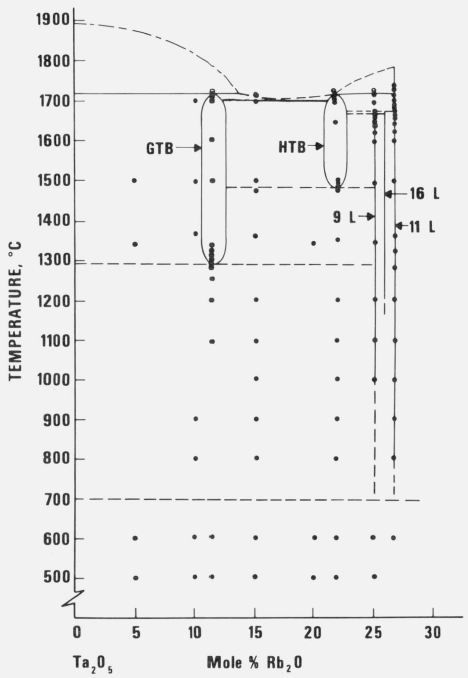


FIGURE 2. *Phase diagram for the system* $Ta_2O_5$:$4Rb_2O$:$11Ta_2O_5$.

## 2.3. Crystal Growth

Many of the phases discovered during the phase equilibria studies of the alkali niobate and tantalate systems have not been previously reported in the literature. One of the objectives of the crystal growth portion of this study has been to synthesize single crystals for x-ray diffraction studies to provide crystallographic information on these materials to assist in the interpretation of x-ray diffraction powder patterns. The second, and equally important objective, has been to grow large single crystals of potentially useful $Rb^+$ phases for use in studies of ion exchange behavior for the purpose of obtaining $Na^+$ and/or $K^+$ analogues.

Table 7. Experimental Data for the System $Ta_2O_5$-$4Rb_2O$:$11Ta_2O_5$.

| Composition | Initial Heat Treatment Temp. °C | Initial Heat Treatment Time hr | Final Heat Treatment[a] Temp. °C | Final Heat Treatment[a] Time hr | Results of Physical Observation | Results of X-ray Diffraction Analysis |
|---|---|---|---|---|---|---|
| $5Rb_2O:95Ta_2O_5$ | | | 500 | 120[b] | | L-$Ta_2O_5$ |
| | 500 | 120 | 600 | 110[b] | | -- |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 1340 | 120 | | L-$Ta_2O_5$ + GTB |
| | | | 1500 | 144 | | H-$Ta_2O_5$ + GTB |
| $10Rb_2O:90Ta_2O_5$ | | | 500 | 120[b] | | -- |
| | 500 | 120 | 600 | 110[b] | | L-$Ta_2O_5$ |
| | 500 | 120 | | | | |
| | 600 | 90 | | | | |
| | | | 800 | 80 | | L-$Ta_2O_5$ + 9L |
| | | | 900 | 60 | | L-$Ta_2O_5$ + 9L |
| | | | 1366 | 120 | | GTB + L-$Ta_2O_5$ |
| | | | 1500 | 120 | | GTB + H-$Ta_2O_5$ (tr) |
| | | | 1700 | 1 | | GTB |
| $11.5Rb_2O:88.5Ta_2O_5$ | | | 500 | 120[b] | | -- |
| | 500 | 120 | 600 | 110[b] | | -- |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 1098 | 136 | | L-$Ta_2O_5$ + 9L |
| | | | 1255 | 27 | | 9L + L-$Ta_2O_5$ |
| | | | 1318 | 16 | | 9L + L-$Ta_2O_5$ |
| | | | 1340 | 120 | | GTB |
| | | | 1500 | 144 | | GTB |
| | | | 1603 | 24 | | GTB |
| | 1200 | 150 | | | | |
| | | | 1296 | 91 | | L-$Ta_2O_5$ + 9L + GTB (tr) |
| | | | 1297 | 117 | | GTB + L-$Ta_2O_5$ |
| | | | 1307 | 64 | | GTB + L-$Ta_2O_5$ |
| | | | 1317 | 67 | | GTB + L-$Ta_2O_5$ |
| | | | 1327 | 18 | | GTB + L-$Ta_2O_5$ |
| | | | 1330 | 115 | | GTB + L-$Ta_2O_5$ |
| | | | 1332 | 16 | | GTB + L-$Ta_2O_5$ |
| | | | 1340 | 72 | | GTB |
| | | | 1704 | 0.5 | not melted | |
| | | | 1709 | 0.5 | not melted | |
| | | | 1714 | .25 | not melted | |
| | | | 1721 | 2 | partially melted | GTB |
| | | | 1722 | 1 | completely melted | |
| | 1330 | 115 | | | | |
| | | | 1317 | 67 | | GTB |
| | 1340 | 72 | | | | |
| | | | 1277 | 136 | | GTB |
| | | | 1297 | 117 | | GTB |
| | 1277 | 136 | | | | |
| | | | 1331 | 115 | | GTB |
| $15Rb_2O:85Ta_2O_5$ | | | 500 | 120[b] | | |
| | 500 | 120 | 600 | 110[b] | | |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 800 | 80 | | L-$Ta_2O_5$ + 9L |
| | | | 900 | 60 | | L-$Ta_2O_5$ + 9L |
| | | | 1000 | 40 | | L-$Ta_2O_5$ + 9L |
| | | | 1098 | 136 | | L-$Ta_2O_5$ + 9L |
| | | | 1360 | 120 | | GTB + 9L |
| | | | 1473 | 65 | | GTB + 9L |
| | | | 1500 | 17.5 | | GTB + HTB |
| | | | 1500 | 18 | | GTB + HTB |
| | | | 1500 | 144 | | GTB + HTB |
| | | | 1700 | 2 | | GTB + HTB |
| | 1200 | 150 | | | | |
| | | | 1707 | 0.5 | not melted | |
| | | | 1711 | 0.5 | not melted | |
| | | | 1714 | 0.5 | completely melted | |
| | | | 1715 | 0.5 | completely melted | |
| $20Rb_2O:80Ta_2O_5$ | | | 500 | 120[b] | | |
| | 500 | 120 | 600 | 110[b] | | |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 1340 | 120 | | 9L + GTB |

In general, the choice of technique was dictated by the characteristics of the desired phase, i.e., congruent or incongruent melting, volatility of one or more of the components, range of coexistence with liquid, and the desired final size of the crystal. Both fluxed melt and Czochralski techniques were utilized, and in some cases, the flux evaporation technique was used for the preparation of small crystals.

## 2.4. Czochralski Crystal Growth

### a. $4Rb_2O:11Nb_2O_5$

A 100 gram batch of $29Rb_2O:71Nb_2O_5$ was calcined at 400 °C for 60 hours for use as a starting material. Five boules were pulled and the remaining charge discarded. The five boules were remelted and used as a "purified" charge

Table 7. Experimental Data for the System $Ta_2O_5$-$4Rb_2O$:$11Ta_2O_5$. (cont.)

| | | | | | | |
|---|---|---|---|---|---|---|
| $21.75Rb_2O$:$78.25Ta_2O_5$ | | | 500 | 120[b/] | | |
| | 500 | 120 | 600 | 110[b/] | | |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 800 | 80 | | 9L + L-$Ta_2O_5$ |
| | | | 900 | 60 | | 9L + L-$Ta_2O_5$ |
| | | | 1000 | 40 | | 9L + L-$Ta_2O_5$ |
| | | | 1100 | 138 | | 9L + L-$Ta_2O_5$ |
| | | | 1360 | 120 | | 9L + GTB |
| | | | 1473 | 65 | | 9L + GTB |
| | | | 1500 | 18 | | 9L + GTB |
| | | | 1643 | 24 | | HTB + 9L (tr) |
| | | | 1700 | 2 | | HTB |
| | | | 1700 | 1 | | HTB |
| | | | 1706 | 1 | | HTB |
| | 1200 | 150 | | | | |
| | | | 1474 | 67 | | 9L + GTB |
| | | | 1477 | 23 | | 9L + GTB |
| | | | 1477 | 18 | | 9L + GTB |
| | | | 1479 | 17 | | 9L + GTB |
| | | | 1479 | 18 | | 9L + GTB |
| | | | 1480 | 17 | | 9L + GTB |
| | | | 1482 | 18 | | 9L + HTB (?) |
| | | | 1482 | 45 | | 9L + GTB |
| | | | 1484 | 20 | | 9L + GTB |
| | | | 1486 | 41 | | 9L + GTB |
| | | | 1488 | 16 | | 9L + HTB |
| | | | 1488 | 16 | | 9L + HTB |
| | | | 1498 | 21 | | 9L + HTB |
| | | | 1706 | 1 | not melted | |
| | | | 1716 | 1 | not melted | HTB |
| | | | 1717 | 0.5 | partially melted | |
| | | | 1721 | 2 | partially melted | HTB |
| $25Rb_2O$:$75Ta_2O_5$ | | | 500 | 120[b/] | | L-$Ta_2O_5$ |
| | 500 | 120 | 600 | 110[b/] | | |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 1000 | 40 | | 9L + L-$Ta_2O_5$ (tr) |
| | | | 1100 | 138 | | 9L |
| | | | 1344 | 120 | | 9L |
| | | | 1498 | 144 | | 9L + ? (tr) |
| | | | 1675 | 18 | | 16L + HTB |
| | | | 1700 | 1 | | 16L + HTB |
| | | | 1700 | 1 | | 16L + HTB |
| | | | 1715 | 1 | not melted | |
| | 1200 | 150 | | | | |
| | | | 1600 | 20 | | 9L |
| | | | 1621 | 3 | | 9L |
| | | | 1624 | 17 | | 9L |
| | | | 1641 | 21 | | 9L |
| | | | 1659 | 19 | | 9L |
| | | | 1663 | 67 | | 9L + HTB (tr) |
| | | | 1677 | 29 | | 9L + HTB + 16L |
| | | | 1682 | 18 | | 16L + HTB |
| | | | 1722 | 16 | partially melted | |
| | | | 1725 | 16 | partially melted | 16L + HTB |
| $26.7Rb_2O$:$73.3Ta_2O_5$ | | | 500 | 120[b/] | | L-$Ta_2O_5$ + 2:3 |
| | 500 | 120 | 600 | 110[b/] | | |
| | 500 | 120 | | | | |
| | 600 | 110 | | | | |
| | | | 800 | 80 | | 11L + 2:3 |
| | | | 900 | 60 | | 11L + 2:3 |
| | | | 1000 | 40 | | 11L + 2:3 |
| | | | 1098 | 136 | | 11L + 2:3 |
| | | | 1360 | 120 | | 16L + 11L |
| | | | 1500 | 120 | | 16L + 11L |
| | | | 1596 | 24 | | 16L + 11L |
| | | | 1625 | 16 | | 16L + 11L |
| | | | 1640 | 2 | | 16L + 11L |
| | | | 1647 | 1 | | 16L + 11L |
| | | | 1700 | 1 | | 11L |
| | | | 1710 | 1 | not melted | |
| | 1200 | 150 | | | | |
| | | | 1283 | 72 | | 16L + 11L |
| | | | 1672 | 1 | | 11L |
| | | | 1719 | 1 | not melted | |
| | | | 1725 | 0.5 | | 11L |
| | | | 1726 | 16 | | 11L |

[a/] Except as indicated by [b/] the samples were quenched into water from the temperature indicated.

[b/] The samples were heated at the temperatures indicated in open Pt crucibles. Due to the volatility of $Rb_2O$ the bulk composition may have shifted to one higher in mole percent $Ta_2O_5$.

## Table 8

X-ray Diffraction Pattern of $11.5Rb_2O:88.5Ta_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 19.66 | 110 | 4.49 | 4.53 | 5 |
| 13.84 | 200 | 6.38 | 6.41 | 5 |
| 12.39 | 210 | 7.13 | 7.16 | 6 |
| 9.77 | 220 | 9.04 | 9.06 | 8 |
| 8.73 | 310 | 10.12 | 10.14 | 6 |
| 7.67 | 320 | 11.53 | 11.56 | 10 |
| 6.70 | 410 | 13.20 | 13.23 | 8 |
| 5.12 | 520 | 17.31 | 17.31 | 3 |
| 4.873 | 440 | 18.19 | 18.19 | 3 |
| 4.731 | 530 | 18.74 | 18.75 | 3 |
| 3.902 | 001 | 22.77 | 22.77 | 100 |
| 3.826 | 111 | 23.23 | 23.23 | 10 |
| 3.754 | 201 | 23.68 | 23.68 | 3 |
| 3.622 | 730 | 24.56 | 24.57 | 23 |
| 3.560 | 311 | 24.99 | 24.98 | 6 |
| 3.531 | 650 | 25.20 | 25.21 | 10 |
| 3.475 | 321 | 25.61 | 25.61 | 8 |
| 3.446 | 800 | 25.83 | 25.83 | 19 |
| 3.422 | 740 | 26.02 | 26.03 | 25 |
| 3.370 | 411 | 26.43 | 26.46 | 10 |
| 3.369 | 331 | 26.63 | 26.63 | 33 |
| 3.250 | 660 | 27.42 | 27.43 | 41 |
| 3.227 | 830 | 27.62 | 27.62 | 39 |
| 3.163 | 511 | 28.19 | 28.18 | 3 |
| 3.045 | 910 | 29.30 | 29.31 | 19 |
| 2.992 | 760 | 29.84 | 29.85 | 29 |
| 2.958 | 611 | 30.19 | 30.20 | 3 |
| 2.924 | 850 | 30.55 | 30.56 | 26 |
| 2.800 | 940 | 31.93 | 31.94 | 10 |
| 2.757 | 860 | 32.45 | 32.45 | 12 |
| 2.731 | 641 | 32.76 | 32.77 | 5 |
| 2.718 | 721 | 32.93 | 32.93 | 5 |
| 2.653 | 731 | 33.75 | 33.75 | 13 |
| 2.617 | 651 | 34.22 | 34.23 | 7 |
| 2.584 | 801 | 34.69 | 34.70 | 10 |
| 2.572 | 741 | 34.86 | 34.86 | 12 |
| 2.540 | 821 | 35.31 | 35.32 | 17 |
| 2.4966 | 661 | 35.94 | 35.94 | 13 |
| 2.4873 | 831 | 36.08 | 36.09 | 12 |
| 2.4006 | 911 | 37.43 | 37.43 | 9 |
| 2.3737 | 761 | 37.87 | 37.87 | 14 |
| 2.3392 | 851 | 38.45 | 38.45 | 15 |
| 2.2744 | 941 | 39.59 | 39.59 | 6 |
| 2.2510 | 861 | 40.02 | 40.01 | 6 |
| 2.1796 | 12,4,0 | 41.39 | 41.39 | 6 |
| 2.1666 | 990 | 41.65 | 41.66 | 3 |
| 2.1152 | 11,7,0 | 42.71 | 42.72 | 3 |
| 2.1091 | 11,0,1 | 42.84 | 42.85 | 3 |
| 1.9497 | 10,10,0 | 46.54 | 46.54 | 27 |
| 1.9259 | 13,6,0 | 47.15 | 47.16 | 8 |
| 1.9027 | 12,4,1 | 47.76 | 47.76 | 5 |
| 1.8934 | 14,4,0 | 48.01 | 48.00 | 14 |
| 1.8542 | 11,10,0 | 49.09 | 49.08 | 13 |
| 1.8339 | 15,1,0 | 49.67 | 49.67 | 6 |
| 1.8060 | 13,8,0 | 50.49 | 50.48 | 14 |
| 1.7723 | 11,11,0 | 51.52 | 51.52 | 4 |
| 1.7437 | 10,10,1/15,5,0 | 52.43 | 52.42/42.43 | 10 |
| 1.7266 | 13,6,1 | 52.99 | 52.98 | 3 |
| 1.7229 | 16,0,0 | 53.11 | 53.10 | 3 |
| 1.7173 | 732 | 53.30 | 53.30 | 3 |
| 1.7066 | 15,6,0 | 53.66 | 53.66 | 5 |
| 1.7031 | 14,4,1 | 53.78 | 53.76 | 8 |
| 1.6984 | 802 | 53.94 | 53.96 | 6 |
| 1.6934 | 12,11,0 | 54.11 | 54.10 | 8 |
| 1.6842 | 13,7,1 | 54.43 | 54.43 | 6 |
| 1.6746 | 11,10,1 | 54.77 | 54.75 | 9 |
| 1.6715 | 16,4,0 | 54.88 | 54.87 | 13 |
| 1.6692 | 832 | 54.96 | 54.95 | 12 |
| 1.6595 | 15,1,1 | 55.31 | 55.30 | 8 |
| 1.6412 | 14,6,1 | 55.98 | 55.95 | 8 |
| 1.6388 | 13,8,1 | 56.07 | 56.06 | 13 |
| 1.6216 | 15,8,0 | 56.72 | 56.71 | 5 |
| 1.6189 | 13,11,0 | 56.82 | 56.82 | 5 |
| 1.6140 | 11,11,1/16,6,0 | 57.01 | 57.02 | 7 |
| 1.6086 | 12,10,1 | 57.22 | 57.24 | 2 |
| 1.5918 | 15,5,1 | 57.88 | 57.87 | 7 |
| 1.5784 | 16,7,0 | 58.42 | 58.40 | 10 |
| 1.5664 | 14,8,1 | 58.92 | 58.92 | 3 |
| 1.5534 | 12,11,1 | 59.45 | 59.44 | 4 |
| 1.5482 | 14,11,0 | 59.67 | 59.66 | 4 |
| 1.5366 | 16,4,1 | 60.17 | 60.18 | 4 |
| 1.4997 | 12,12,1/17,7,0 | 61.81 | 61.80/61.81 | 3 |
| 1.4979 | 15,8,1 | 61.89 | 61.90 | 3 |
| 1.4952 | 14,12,0 | 62.02 | 62.00 | 7 |
| 1.4627 | 16,7,1 | 63.55 | 63.52 | 7 |
| 1.4611 | 16,10,0 | 63.63 | 63.62 | 6 |
| 1.4389 | 14,11,1 | 64.73 | 64.71 | 4 |
| 1.4336 | 11,7,2/16,8,1/ 19,3,0 | 65.00 | 64.99/65.00/ 65.01 | 2 |
| 1.3996 | 18,8,0 | 66.78 | 66.77 | 3 |
| 1.3844 | 14,1,2 | 67.61 | 67.62 | 3 |
| 1.3688 | 16,10,1 | 68.49 | 68.51 | 4 |
| 1.3583 | 19,1,1 | 69.09 | 69.09 | 5 |
| 1.3534 | 19,2,1 | 69.38 | 69.37 | 4 |
| 1.3435 | 15,14,0 | 69.97 | 69.95 | 4 |
| 1.3404 | 18,7,1 | 70.15 | 70.13 | 3 |
| 1.3359 | 15,1,2 | 70.42 | 70.40 | 4 |
| 1.3248 | 17,12,0 | 71.10 | 71.09 | 4 |
| 1.3155 | 16,12,1/15,15,0 | 72.68 | 72.68/72.69 | 5 |

[a/] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1340°C for 72 hours and quenched into water.

[b/] This diffraction pattern was indexed with the aid of the single crystal pattern of the $11.5K_2O:88.5Nb_2O_5$ analogue on the basis of a tetragonal unit cell with a=27.57±.007Å and c=3.9018±.0005Å.

Table 9

X-ray Diffraction Powder Pattern of $21.75Rb_2O:78.25Ta_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 6.52 | 100 | 13.56 | 13.57 | 31 |
| 3.907 | 001 | 22.74 | 22.74 | 29 |
| 3.768 | 110 | 23.59 | 23.61 | 3 |
| 3.35 | 101 | 26.57 | 26.57 | 38 |
| 3.26 | 200 | 27.34 | 27.33 | 100 |
| 2.71 | 111 | 33.02 | 33.01 | 41 |
| 2.50 | 201 | 35.85 | 35.84 | 52 |
| 2.4663 | 210 | 36.40 | 36.42 | 7 |
| 2.1752 | 300 | 41.48 | 41.51 | 4 |
| 2.0851 | 211 | 43.36 | 43.37 | 14 |
| 1.9542 | 002 | 46.43 | 46.44 | 21 |
| 1.8998 | 301 | 47.84 | 47.84 | 21 |
| 1.8824 | 220 | 48.31 | 48.30 | 40 |
| 1.8719 | 102 | 48.60 | 48.61 | 5 |
| 1.8088 | 310 | 50.41 | 50.41 | 6 |
| 1.6962 | 221 | 54.02 | 54.02 | 19 |
| 1.6761 | 202 | 54.72 | 54.73 | 26 |
| 1.6416 | 311 | 55.97 | 55.98 | 11 |
| 1.6304 | 400 | 56.39 | 56.39 | 18 |
| 1.5304 | 212 | 60.44 | 60.41 | 4 |
| 1.5046 | 401 | 61.59 | 61.59 | 18 |
| 1.4958 | 320 | 61.99 | 61.97 | 2 |
| 1.3973 | 321 | 66.91 | 66.91 | 9 |
| 1.3555 | 222 | 69.26 | 69.25 | 16 |
| 1.3370 | 411 | 70.36 | 70.35 | 5 |
| 1.3271 | 312 | 70.96 | 70.95 | 3 |
| 1.2769 | 103 | 74.21 | 74.19 | 2 |

[a/] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1706°C for 1 hour and quenched into water.

[b/] This diffraction pattern was indexed with the aid of single crystal precession patterns on the basis of a hexagonal unit cell with a=7.5306±.0005A and c=3.9072±.0005A.

for the actual crystal growth experiments. From this "purified" charge large, clear single crystal boules of the "11-layer" phase were grown. The "11-layer" crystals show a marked preference for growth perpendicular to the *c* axis and at least one excellent cleavage (basal-plane) is evident. Density measurements made with a double pan liquid displacement apparatus gave a value of $4.40 \pm .05$ g/cm$^3$.

### b. $21.75Rb_2O$: $78.25Nb_2O_5$ (HTB)

Crystals of the hexagonal tungsten bronze (HTB) phase in this system were grown by pulling from a melt of the composition $21.75Rb_2O:78.25Nb_2O_5$ (experiments performed at NBS by C. Jones as part of the American University Research Participation Program). Large, clear, water-white crystals were easily obtained but all fractured into large blocks during cooling. The fracture may be related to a non-quenchable symmetry change from a high temperature hexagonal form to the room temperature orthorhombic form, or to extreme anisotropy of thermal expansion.

### c. $11.5Rb_2O$:$88.5Nb_2O_5$ (GTB)

Crystals of the Gatehouse tetragonal bronze (GTB) phase were grown from a composition of $16Rb_2O:84Nb_2O_5$ (experiments performed by D. Klein at NBS as part of the American University Research Participation Program). Small single crystal boules were successfully pulled from the melt, but again fractures developed during cooling.

## Table 10

X-ray Diffraction Powder Pattern of the "9-L" Phase Occurring at the Composition $Rb_2O:3Ta_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 9.13 | 004 | 9.68 | 9.71 | 19 |
| 6.51 | 100 | 13.59 | 13.61 | 70 |
| 6.40 | 101 | 13.82 | 13.80 | 9 |
| 6.08 | 006 | 14.56 | 14.59 | 6 |
| 5.74 | 103 | 15.43 | 15.45 | 14 |
| 4.855 | 105 | 18.26 | 18.28 | 9 |
| 4.568 | 008 | 19.46 | 19.49 | 12 |
| 3.729 | 108 | 23.84 | 23.85 | 7 |
| 3.678 | 112 | 24.18 | 24.19 | 3 |
| 3.472 | 114 | 25.64 | 25.65 | 45 |
| 3.431 | 109 | 25.96 | 25.92 | 80 |
| 3.252 | 200 | 27.40 | 27.41 | 46 |
| 3.237 | 201 | 27.53 | 27.52 | 63 |
| 3.194 | 116 | 27.91 | 27.93 | 35 |
| 3.137 | 203 | 28.43 | 28.40 | 100 |
| 3.061 | 204 | 29.15 | 29.14 | 33 |
| 3.033 | 0,0,12 | 29.43 | 29.42 | 29 |
| 2.968 | 205 | 30.08 | 30.08 | 65 |
| 2.896 | 118 | 30.85 | 30.85 | 47 |
| 2.867 | 206 | 31.17 | 31.19 | 12 |
| 2.759 | 207 | 32.42 | 32.45 | 6 |
| 2.752 | 119 | 32.51 | 32.51 | 12 |
| 2.748 | 1,0,12 | 32.56 | 32.54 | 12 |
| 2.646 | 208 | 33.85 | 33.86 | 27 |
| 2.601 | 0,0,14 | 34.45 | 34.46 | 9 |
| 2.534 | 209 | 35.40 | 35.39 | 50 |
| 2.4576 | 210 | 36.53 | 36.53 | 13 |
| 2.4531 | 211 | 36.60 | 36.62 | 10 |
| 2.4144 | 1,0,14 | 37.21 | 37.21 | 6 |
| 2.3588 | 1,1,12 | 38.12 | 38.11 | 5 |
| 2.3306 | 215 | 38.60 | 38.64 | 4 |
| 2.2176 | 2,0,12 | 40.65 | 40.64 | 4 |
| 2.1671 | 300 | 41.64 | 41.64 | 2 |
| 2.1626 | 301 | 41.73 | 41.72 | 2 |
| 2.1210 | 2,0,13 | 42.59 | 42.57 | 7 |
| 2.1097 | 304 | 42.83 | 42.86 | 12 |
| 2.1001 | 219 | 43.02 | 43.03 | 17 |
| 2.0779 | 305 | 43.52 | 43.53 | 2 |
| 2.0417 | 306 | 44.33 | 44.35 | 8 |
| 2.0364 | 2,1,10 | 44.45 | 44.44 | 8 |
| 2.0222 | 0,0,18 | 44.78 | 44.77 | 21 |
| 1.9562 | 308 | 46.38 | 46.37 | 17 |
| 1.9446 | 2,0,15 | 46.67 | 46.66 | 7 |
| 1.9096 | 2,1,12 | 47.58 | 47.58 | 9 |
| 1.8759 | 220 | 48.49 | 48.46 | 79 |
| 1.8635 | 2,0,16 | 48.83 | 48.81 | 3 |
| 1.8388 | 224/1,0,19 | 49.53 | 49.55/49.55 | 6 |
| 1.8031 | 310 | 50.58 | 50.57 | 7 |
| 1.7941 | 312/226 | 50.85 | 50.84/50.88 | 5 |
| 1.7875 | 2,0,17 | 51.05 | 51.03 | 27 |
| 1.7859 | 2,1,14 | 51.10 | 51.10 | 26 |
| 1.7843 | 313 | 51.15 | 51.17 | 21 |
| 1.7628 | 3,0,12 | 51.82 | 51.80 | 3 |
| 1.7352 | 228 | 52.71 | 52.71 | 5 |
| 1.7174 | 2,0,18 | 53.30 | 53.30 | 12 |
| 1.7150 | 3,0,13 | 53.38 | 53.41 | 13 |
| 1.6752 | 1,0,21 | 54.75 | 54.75 | 2 |
| 1.6678 | 2,2,10 | 55.01 | 55.00 | 2 |
| 1.6540 | 0,0,22 | 55.51 | 55.48 | 2 |
| 1.6467 | 319 | 55.78 | 55.77 | 16 |
| 1.6252 | 400 | 56.58 | 56.57 | 9 |
| 1.6239 | 401 | 56.63 | 56.64 | 8 |
| 1.6110 | 403 | 57.13 | 57.13 | 13 |
| 1.5999 | 404 | 57.56 | 57.55 | 10 |
| 1.5962 | 2,2,12 | 57.71 | 57.71 | 20 |
| 1.5864 | 405 | 58.10 | 58.10 | 11 |
| 1.5703 | 406 | 58.75 | 58.76 | 3 |
| 1.5410 | 3,1,12 | 59.60 | 59.59 | 5 |
| 1.5303 | 408 | 60.44 | 60.42 | 14 |
| 1.5287 | 2,0,21 | 60.51 | 60.47 | 21 |
| 1.5221 | 2,2,14 | 60.80 | 60.81 | 12 |
| 1.5080 | 409 | 61.43 | 61.42 | 15 |
| 1.4912 | 320 | 62.20 | 62.18 | 3 |
| 1.4816 | 3,1,14 | 62.65 | 62.64 | 5 |
| 1.4805 | 323 | 62.70 | 62.70 | 5 |
| 1.4778 | 1,0,24 | 62.83 | 62.85 | 5 |
| 1.4592 | 4,0,11 | 63.72 | 63.73 | 2 |
| 1.4223 | 2,0,23 | 65.58 | 65.54 | 3 |
| 1.4192 | 0,0,26 | 66.74 | 66.75 | 5 |
| 1.3989 | 329 | 66.82 | 66.79 | 11 |
| 1.3783 | 4,0,14 | 67.95 | 67.95 | 4 |
| 1.3753 | 2,2,18/2,0,24 | 68.12 | 68.09/68.16 | 18 |
| 1.3544 | 418 | 69.32 | 69.32 | 6 |
| 1.3382 | 3,2,12 | 70.28 | 70.26 | 3 |
| 1.3219 | 4,1,10 | 71.28 | 71.28 | 3 |
| 1.2940 | 3,2,14 | 73.06 | 73.07 | 8 |

[a/] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1659°C for 16 hours and quenched into water.

[b/] This diffraction pattern was indexed with the aid of single crystal precession patterns on the basis of a hexagonal unit cell with a=7.5078±.0006Å and c=36.408±.005Å.

## Table 11

X-ray Diffraction Powder Pattern of $4Rb_2O:11Ta_2O_5$.[a/]

| $d_{obs}$ | hkℓ | $2\theta_{obs}$ | $2\theta_{calc}$[b/] | $I_{obs}$ |
|---|---|---|---|---|
| 14.43 | 003 | 6.12 | 6.13 | 5 |
| 7.20 | 006 | 12.28 | 12.28 | 20 |
| 6.43 | 101 | 13.75 | 13.76 | 30 |
| 6.23 | 102 | 14.20 | 14.22 | 5 |
| 5.57 | 104 | 15.90 | 15.90 | 16 |
| 5.18 | 105 | 17.05 | 17.06 | 2 |
| 4.800 | 009 | 18.47 | 18.47 | 3 |
| 4.157 | 108 | 21.36 | 21.38 | 6 |
| 3.632 | 113 | 24.49 | 24.49 | 10 |
| 3.599 | 0,0,12/1,0,10 | 24.72 | 24.71/24.73 | 10 |
| 3.357 | 1,0,11 | 26.53 | 26.50 | 44 |
| 3.326 | 116 | 26.78 | 26.77 | 59 |
| 3.240 | 201 | 27.51 | 27.50 | 23 |
| 3.217 | 202 | 27.71 | 27.73 | 4 |
| 3.149 | 1,0,12 | 28.32 | 28.32 | 4 |
| 3.112 | 204 | 28.66 | 28.66 | 17 |
| 3.041 | 205 | 29.35 | 29.33 | 100 |
| 2.956 | 1,0,13 | 30.21 | 30.18 | 20 |
| 2.881 | 0,0,15 | 31.02 | 31.03 | 35 |
| 2.787 | 1,0,14 | 32.08 | 32.09 | 12 |
| 2.597 | 2,0,10 | 34.51 | 34.51 | 38 |
| 2.504 | 2,0,11 | 35.84 | 35.83 | 8 |
| 2.4941 | 1,0,16 | 35.98 | 35.99 | 8 |
| 2.4532 | 211 | 36.60 | 36.60 | 5 |
| 2.4013 | 0,0,18 | 37.42 | 37.45 | 4 |
| 2.3952 | 214 | 37.52 | 37.51 | 4 |
| 2.3237 | 2,0,13 | 38.72 | 38.72 | 2 |
| 2.2840 | 1,1,15 | 39.42 | 39.41 | 4 |
| 2.2512 | 1,0,18 | 40.02 | 40.02 | 1 |
| 2.2367 | 218 | 40.29 | 40.30 | 3 |
| 2.1461 | 1,0,19 | 42.07 | 42.07 | 4 |
| 2.1436 | 303 | 42.12 | 42.14 | 5 |
| 2.0829 | 2,1,11 | 43.41 | 43.41 | 11 |
| 2.0756 | 306 | 43.57 | 43.58 | 19 |
| 2.0567 | 0,0,21 | 43.99 | 43.99 | 17 |
| 2.0453 | 307 | 44.26 | 44.27 | 3 |
| 2.0201 | 1,1,18 | 44.83 | 44.79 | 3 |
| 2.0019 | 2,0,17 | 45.26 | 45.26 | 3 |
| 1.9747 | 309 | 45.92 | 45.91 | 7 |
| 1.9218 | 2,1,14 | 47.26 | 47.25 | 7 |
| 1.8762 | 220 | 48.48 | 48.47 | 38 |
| 1.8614 | 223 | 48.89 | 48.91 | 3 |
| 1.8162 | 226 | 50.19 | 50.20 | 12 |
| 1.8028 | 310 | 50.59 | 50.58 | 15 |
| 1.7988 | 2,0,20 | 50.71 | 50.71 | 29 |
| 1.7776 | 314 | 51.36 | 51.33 | 3 |
| 1.7660 | 2,1,17 | 51.72 | 51.71 | 3 |
| 1.7478 | 229 | 52.30 | 52.30 | 2 |
| 1.6682 | 2,2,12 | 55.00 | 54.98 | 2 |
| 1.6638 | 3,1,10 | 55.16 | 55.16 | 3 |
| 1.6377 | 3,1,11 | 56.11 | 56.08 | 8 |
| 1.6234 | 1,1,24 | 56.65 | 56.68 | 6 |
| 1.6092 | 1,0,26 | 57.20 | 57.18 | 6 |
| 1.5963 | 405 | 57.70 | 57.67 | 18 |
| 1.5712 | 407 | 58.71 | 58.70 | 27 |
| 1.5564 | 408 | 59.33 | 59.34 | 4 |
| 1.5331 | 2,1,22 | 60.32 | 60.29 | 2 |
| 1.5251 | 2,0,25 | 60.67 | 60.65 | 12 |
| 1.5208 | 4,0,10 | 60.86 | 60.85 | 15 |
| 1.4986 | 3,1,16 | 61.86 | 61.83 | 6 |
| 1.4903 | 321 | 62.24 | 62.24 | 7 |
| 1.4786 | 2,2,18 | 62.79 | 62.81 | 9 |
| 1.4393 | 0,0,30 | 64.71 | 64.69 | 5 |
| 1.4357 | 2,0,27 | 64.89 | 64.91 | 4 |
| 1.3932 | 0,0,31 | 67.13 | 67.12 | 6 |
| 1.3911 | 416 | 67.24 | 67.21 | 10 |
| 1.3859 | 2,2,21 | 67.53 | 67.51 | 9 |
| 1.3758 | 2,1,26 | 68.09 | 68.07 | 4 |
| 1.3608 | 419 | 68.95 | 68.98 | 3 |
| 1.3422 | 3,2,14 | 70.04 | 70.01 | 2 |
| 1.2980 | 502 | 72.80 | 72.82 | 8 |

[a/] This powder diffraction pattern was obtained from material heated in a sealed Pt tube at 1719°C for 1 hour and quenched into water.

[b/] This diffraction pattern was indexed with the aid of single crystal precession patterns on the basis of a hexagonal unit cell with a=7.5065±.0007Å and c=43.194±.005Å, h+k+ℓ=3n.

## 2.5 Flux Evaporation Crystal Growth

### a. The Systems $Rb_2O$-$Nb_2O_5$ and $Rb_2O$-$Ta_2O_5$ With $MoO_3$

Nine different compositions of two grams each were prepared from $Rb_2CO_3$, $Nb_2O_5$, and $MoO_3$. These samples were placed in 5 mL Pt crucibles and heated to 900–1100 °C in an induction furnace. Small crystals (~2 mm) of the "11-layer" phase were obtained from compositions of 30:5:65 and 30:10:60 ($Rb_2O$:$Nb_2O_5$:$MoO_3$). A 27.5:10:62.5 composition yielded small crystals of the GTB phase plus H-$Nb_2O_5$ while a 28:6:67 composition yielded single crystals of the HTB phase. No crystals of the unidentified phase occurring at about 15 mol per cent $Rb_2O$ were obtained by the flux evaporation technique.

Six different compositions in the $Rb_2O$-$Ta_2O_5$-$MoO_3$ system were prepared and heated as in the $Rb_2O$-$Nb_2O_5$-$MoO_3$ system. The 30:10:60 and 35:5:60 compositions when heated to 1100 °C yielded single crystals of the "9-layer" phase. No other compositions yielded crystals of phases found in the subsystem being studied.

### b. The System $Rb_2O$:$Ta_2O_5$:RbF

In view of the success obtained by the flux evaporation synthesis route using KF in the $KSbO_3$-KF system [8], similar attempts were made using RbF and $Ta_2O_5$ in an attempt to obtain rubidium tantalate crystals. However, $RbTa_2O_5$ with the pyrochlore structure was the only identified product. A 95RbF:5$Ta_2O_5$ composition was completely liquid at 925 °C and on cooling yielded acicular crystals of an unknown phase. Clear, euhedral octahedra of the $RbTa_2O_5F$ pyrochlore were obtained from a composition of 75RbF:25$Ta_2O_5$ heated to about 1150 °C for 30 seconds.

## 2.6. Ion Exchange

One of the best screening tests for the ionic conductivity of a solid phase is to determine whether or not the alkali ion in the structure can be exchanged with a different alkali ion. This may be tested by heating in a large excess of a molten salt (or solution) containing the second ion. A large number of experiments of this type were performed on many different compounds found in this study. In this paper, the terms "single ion exchange" and "double ion exchange" refer to the exchange of $K^+$ or $Na^+$ for $Rb^+$ and the sequential exchange of $K^+$ for $Rb^+$ followed by $Na^+$ for $K^+$, respectively. The results of these tests are found in table 12.

Most of the exchange experiments have been performed on powdered materials. In those cases where single crystals could be grown either by Czochralski or flux evaporation, attempts were made to ion exchange the single crystals.

In general, the results of ion exchange experiments on single crystals were disappointing in that either disruption of the single crystal occurred or exchange proceeded at extremely low rates.

Ion exchange experiments were conducted in the $Rb_2O$-$Nb_2O_5$ system with particular emphasis on the "11-layer" compound occurring at or about 26.67 mol per cent $Rb_2O$. Ion exchange experiments were conducted on both single

Table 12a. Summary of Ion Exchange Experiments

| Exchange Media | Temp °C | Time hrs | Results |
|---|---|---|---|
| | $4Rb_2O:11Nb_2O_5$ [a] | | |
| | Single Exchange | | |
| $KNO_3$ | 400 | 3 | K exch. "11-L" phase a=7.554, c=43.398 |
| $KNO_3$ | 400 | 16 | K exch. "11-L" phase |
| $KNO_3$ | 400 | 16 | K exch. "11-L" phase |
| $KNO_3$ | 450 | 36 | K exch. "11-L" phase |
| $NaNO_3$ | 500 | 1 | Partially exch. a=7.4, c=43.6 |
| $NaNO_3$ | 450 | 64 | Partially decomposed |
| $NaNO_3$ | 414 | 17 | Partially exch. a=7.458, c=43.19 |
| $NaNO_3$ | 400 | 16 | Partially exch. a=7.472, c=43.23 |
| | Double Exchange | | |
| $KNO_3$ | 400 | 3 | |
| $NaNO_3$ | 400 | 1.5 | a=7.458 c=43.398 |
| $NaNO_3$ | 400 | 16 | a=7.368 c=43.869 |
| $KNO_3$ | 400 | 16 | |
| $NaNO_3$ | 450 | 66 | a=7.366 c=43.898 |
| $KNO_3$ | 400 | 16 | |
| $NaNO_3$ | 450 | 98 | a=7.332 c=43.997 |
| | $Rb_2O:3Nb_2O_5$ | | |
| | Single Exchange | | |
| $KNO_3$ | 450 | 3 | K exch. "9-L" phase a=7.56, c=36.52 |
| | $21.75Rb_2O:78.25Nb_2O_5$ [a] | | |
| | Single Exchange | | |
| $KNO_3$ | 450 | 18 | No exchange |
| $KNO_3$ | 450 | 99 | |
| $NaNO_3$ | 450 | 99 | Partial exch., increase in "c" and partial decomposition |
| | Double Exchange | | |
| $KNO_3$ | 450 | 18 | |
| $NaNO_3$ | 450 | 23 | Partial exch. |
| | $RbTa_2O_5F$ | | |
| | Single Exchange | | |
| $KNO_3$ | 340 | 2.5 | Partial exch. a=7.512, c=3.879 |
| $KNO_3$ | 340 | 15 | Partial exch. a=7.512, c=3.879 |
| $KNO_3$ | 450 | 16 | Partial exch. a=7.512, c=3.879 |
| $NaNO_3$ | 340 | 3.5 | No exchange |
| | Double Exchange | | |
| $KNO_3$ | 450 | 16 | |
| $NaNO_3$ | 340 | 2 | No exchange |
| $KNO_3$ | 450 | 16 | |
| $NaNO_3$ | 450 | 44.5 | Some decomposition, partial exchange a=7.51, c=3.814 |
| | $Rb_{1-5x}Nb_{3.4+x}O_9$ | | |
| | Single Exchange | | |
| $NaNO_3$ | 500 | 2 | Unchange HTB+$Na_2Nb_4O_{11}$(tr) + $NaNbO_3$ (tr) |
| $NaNO_3$ | 330 | 2 | No change |
| $3NaNO_2$:$2NaNO_3$ | 240 | 22 | No change |
| $KNO_3$ | 500 | 2 | $KNbO_3$ + unchange HTB |

[a] Single crystal fragments

Table 12b. Summary of Ion Exchange Experiments with $4Rb_2O:11Nb_2O_5$ Pellets

| Starting Material | Pressing History | Firing History | $K^+$ Exchange History | $Na^+$ Exchange History | Remarks |
|---|---|---|---|---|---|
| $4Rb_2O:11Nb_2O_5$ 500°C-90 hr[c/] | 10000 psi[a/] 20000 psi[b/] | 1200°-7 hr | | | Pellets cracked during firing $a$=7.522 $c$=43.180 |
| | | | $KNO_3$-20 hr @ 400° partial exchange[e/] | | Pellet fragment disintegrated $a$=7128, $c$=43.469 |
| | | ↑15°/hr 1200°-7 hr | $KNO_3$-16 hr @400° partial exchange | $NaNO_3$-18 hr @400°C Partial exchange | Pellet fragment did not disintegrate $K^+$ $a$=7.575, $c$=43.469 $Na^+$ $a$=7.390, $c$=43.663 |
| | | ↑5°/minute 1200°-1 hr ↓5°/minute | $KNO_3$-1 hr @400° complete exchange | | Pellet did not disintegrate $K^+$ $a$=7.545, $c$=43.332 |
| | | ↑3°/minute 1200°-1 hr ↓3°/minute | $KNO_3$-19 hr @400° complete exchange | | Pellet displayed some spalling $K^+$ $a$=7.555 $c$=43.428 |
| 500-120 hr 600-90 hr[d/] | 10000 psi[a/] | 1100°-1 hr | $KNO_3$-16 hr @400° complete exchange | $NaNO_3$-21 hr @400° | $K^+$ $a$=7.551, $c$=43.401 $Na^+$ cells not calculated due to broadness of lines in diffraction |
| | | 1100°-1.5 hr | $KNO_3$-16 hr @400° partial exchange | $NaNO_3$-41 hr @400° partial exchange | Na exchanged pellet decomposed $K^+$ $a$=7.547, $c$=43.428 $Na^+$ $a$=7.404, $c$=43.332 |
| | | 1100°-1 hr | $KNO_3$-72 hr @400° complete exchange | $NaNO_3$-32 hr @400° partial exchange | $K^+$ $a$=7.557, $c$=43.442 $Na^+$ $a$=7.484, $c$=43.482 |
| | 10000 psi[a/] 20000 psi[b/] | 1100°-1 hr 1200°-1 hr 1100°-16 hr 1200°-2 hr | $KNO_3$-16 hr @400° complete exchange | | Pellet cracked during final 1200° firing $K^+$ $a$=7.557 $c$=43.442 |
| 500-90 hr | | ↑5°/minute 1200°-5 hr ↓5°/minute | $KNO_3$-2 hr @400° complete exchange | | Powder fired in open tube $K^+$ $a$=7.549, $c$=43.387 |
| | | | $KNO_3$-18 hr[d/] @400° complete exchange | $NaNO_3$-18 hr @400° complete exchange | $K^+$ $a$=7.553, $c$=43.387 $Na^+$ $a$=7.375, $c$=43.830 |

[a/] pressed in steel dies

[b/] isostatic pressing

[c/] without PVA binder

[d/] with PVA binder

[e/] complete exchange

| | a | c |
|---|---|---|
| $4Rb_2O:11Nb_2O_5$ = | 7.522Å | 43.180Å |
| $K^+$ exchanged product = | 7.554Å | 43.398Å |
| $Na^+$ exchanged product = | 7.368Å | 43.869Å |

crystal fragments obtained from crystals grown from the melt and low temperature calcines of 4:11 powders. The single crystals underwent $K^+$ exchange in molten $KNO_3$ but disintegrated during $Na^+$ exchange in $NaNO_3$ during various temperature and time combinations. Pellets of the "11-L" phase were pressed both uniaxially and isostatically with and without polyvinyl alcohol binder, fired and x-ray diffraction powder patterns made before any attempt was made to exchange. Generally the $K^+$ exchange occurred without too much degradation of the specimen but the pellets disintegrated to a fine powder during $Na^+$ exchange. The unit cell dimensions for complete ion exchange (table 12) were developed from the results of ion exchange in molten salts from very small single crystal fragments.

## 3. Relation of Structural Mechanisms of Non-stoichiometry to Ionic Conductivity

It is probably generally accepted that a phase which exhibits unusual ionic conductivity must necessarily be structurally non-stoichiometric. Unfortunately the opposite is not necessarily true. For this reason it is worthwhile to discuss the nature of the non-stoichiometry which has been observed in this study for those phases which seem to be of interest.

### 3.1. Hexagonal Tungsten Bronze-type Phases (HTB)

It has already been reported [2, 5] that the hexagonal tungsten bronze-type phase (HTB) found in binary alkali niobate and tantalate systems has alkali ions in non-stoichiometric positions and excess $Nb^{+5}$ or $Ta^{+5}$ ions. These excess pentavalent ions may well block the alkali ion conductivity as these hexagonal bronzes cannot be ion exchanged. There are two mechanisms that have proved effective in altering the ion exchange characteristics of the hexagonal tungsten bronze-type structures. One is to change the total alkali:other cation valence ratio by substituting $W^{+6}$ for $Ta^{+5}$, for instance in the system $KTaO_3$-$WO_3$ [1]. The alternate to replacing $Ta^{+5}$ ions with $W^{+6}$ ions is to change the structure enough to allow ion exchange (see sec. 3.3).

### 3.2. Pyrochlore Phases

The pyrochlore structural formula should be written as $[A_2X]\,[B_2X_6]$. The $RbTa_2O_5F$ is apparently equivalent to the formula

$$[\square_2 Rb]^{+1}\,[Ta_2O_5F]^{-1}$$

as shown by the structural study of single crystals [9] prepared by the flux synthesis method described by the present authors [2]. The $Rb^+$ ion is apparently too large for the A sites and it is this preference for the larger anion (X) site that makes this compound stable. During ion exchange in $KNO_3$ the $K^+$ ion apparently enters the A site and, upon exposure to atmospheric moisture, an $H_2O$ molecule occupies the (X) site formerly containing $Rb^+$. The formula is then

$$[\square K\ H_2O]^{+1}\,[Ta_2O_5F]^{-1}.$$

During sodium exchange it is apparently possible to obtain a non-stoichiometric amount of sodium in this lattice. The formula for this phase might be postulated as

$$[Na_{1+x}OH_x]^{+1}\,[Ta_2O_5F]^{-1}.$$

The product obtained by acid leaching of this pyrochlore might then be

$$[\square_2 H_3O]^{+1}\,[Ta_2O_5F]^{-1}.$$

The differences in these formulas seem to be related to the size of the monovalent ions entering the ion exchangeable positions. Although infrared analysis of the $Na^+$ exchange product does not indicate $(OH)^-$ [9] it would probably be worthwhile to examine this product with NMR for hydrogen resonance, a much more sensitive method than infrared absorption.

### 3.3. Hexagonal Tungsten Bronze-Pyrochlore Series

The $[B_2X_6]$ framework of the pyrochlore structure can be described as consisting of alternating layers of the hexagonal tungsten bronze structure separated by layers of isolated octahedra sharing only two corners with the adjacent HTB layers. If this structure is modified by increasing the sequence number of either of these types of layers from the cubic packing of AaBbCc to any other arrangement, a sequence of hexagonal phases would be formed having the same *a* axis as the HTB structure and with varying but integral multiplicities of the *c* axis dimension. Such phases are actually encountered in the $K_2O$-$Ta_2O_5$ [1], $Rb_2O$-$Nb_2O_5$ and $Rb_2O$-$Ta_2O_5$ [2] systems and had been estimated by us to represent "9-layer", "16-layer", and "11-layer" sequences. All of the phases can be ion exchanged by $K^+$ and $Na^+$ unlike the HTB phases in the same systems. The reason for this appears to be that a rotation or translation of a portion of the layer sequence allows the isolated vertical channels found in the HTB structure to be changed to intersecting channels as in the cubic pyrochlore structure. Unfortunately, however, the $Na^+$ ion exchanged products are not stable above about 450 °C.

As in the case with the pyrochlore compounds, the $K_2O$ containing phases have unit cell dimensions very similar to or even larger than the corresponding $Rb_2O$ containing phases (table 13). For instance the *c* axis for the "11-layer" phase in the $K_2O$-$Ta_2O_5$ system is 43.512 A while that in the $Rb_2O$-$Nb_2O_5$ system is 43.18 A and in the $Rb_2O$-$Ta_2O_5$ system it is 43.19 A. This may be due to a real difference in total alkali content. It may also be due to hydration of the $K_2O$ phases. No high temperature x-ray data is available to check this hypothesis but small single crystals of the 2:5 $K_2O$:$Ta_2O_5$ phase have been noted to crack, spall and jump on exposure to air.

A mechanism of structural chemistry applicable to these phases was first described by Gatehouse [10] for a crystal of a metastable phase prepared in this laboratory [1] in the $K_2O$-$Ta_2O_5$ system and called metastable $K_2O$:$3Ta_2O_5$. Gatehouse has shown that a rotation or translation of one layer of hexagonal bronze can fit into another so that a basic unit is formed with one set of three corner shared octahedra lying above a second set of three corner shared octahedra, each octahedra sharing two edges with the second set. The ideal

Table 13. Unit Cell Data for Phases Found in the $Ta_2O_5$-$KTaO_3$, $Nb_2O_5$-$4Rb_2O$:$11Nb_2O_5$, and $Ta_2O_5$-$4Rb_2O$:$Ta_2O_5$ Systems.

| System | Designation | Composition Mole % | | Symmetry | Unit Cell Dimension a Å | b Å | c Å | β | Conditions Limiting Possible Reflections | Probable Space Group |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $Rb_2O$ | $Nb_2O_5$ | | | | | | | |
| $Rb_2O$-$Nb_2O_5$ | 11-L | 26.67 | 73.33 | Hexagonal | 7.522 | - | 43.18 | - | hkℓ:-h+k+ℓ=3n | R3,R$\bar{3}$,R32,R3m,R$\bar{3}$m |
| | 16-L | 25.5 | 74.5 | Hexagonal | 7.514 | - | 65.12 | - | hhℓ:ℓ=2n | P6$_3$mc,P$\bar{6}$2c,P6$_3$mmc |
| | 9-L | 25 | 75 | Hexagonal | 7.518 | - | 36.353 | - | hhℓ:ℓ=2n | P6$_3$mc,P$\bar{6}$2c,P6$_3$mmc |
| | HTB | 21.75 | 78.25 | Orthorhombic | 12.991 | 7.550 | 7.796 | - | hk0:h+k=2n<br>h0ℓ:ℓ=2n | Pmcn |
| | GTB | 11.5 | 88.5 | Tetragonal | 27.484 | - | 3.9757 | - | h00:h=2n | P42$_1$2,P$\bar{4}$2$_1$m |
| | | $Rb_2O$ | $Ta_2O_5$ | | | | | | | |
| $Rb_2O$-$Ta_2O_5$ | 11-L | 26.67 | 73.33 | Hexagonal | 7.506 | - | 43.19 | - | hkℓ:-h+k+ℓ=3n | R3,R$\bar{3}$,R32,R3m,R$\bar{3}$m |
| | 9-L | 25 | 75 | Hexagonal | 7.508 | - | 36.41 | - | hhℓ:ℓ=2n | P6$_3$mc,P$\bar{6}$2c,P6$_3$mmc |
| | HTB | 21.75 | 78.25 | Hexagonal | 7.531 | - | 3.907 | - | none | P6/mmm |
| | GTB | 11.5 | 88.5 | Tetragonal | 27.573 | - | 3.9018 | - | h00:h=2n | P42$_1$,2,P$\bar{4}$2$_1$m |
| | | $Ta_2O_5$ | $K_2O$ | | | | | | | |
| $Ta_2O_5$-$KTaO_3$ | GTB | 88.5 | 11.5 | Tetragonal | 27.55 | - | 3.899 | - | h00:h=2n | P42$_1$2,P42$_1$m |
| | 1:5 | 83.33 | 16.67 | Orthorhombic | 5.654 | 10.713 | 16.80 | - | h0ℓ:ℓ=2n<br>0kℓ:k=2n | Pbcm,Pbc2$_1$ |
| | TTBs | 80 | 20 | Orthorhombic | 12.547 | 37.641 | 3.922 | - | h0ℓ:h=2n | Pmam,P2$_1$am,Pma2 |
| | HTB | 78.25 | 21.75 | Hexagonal | 7.527 | - | 3.901 | - | none | P6mmm |
| | 9L | 73.85 | 26.15 | Hexagonal | 7.55 | - | 36.583 | - | hhℓ:ℓ=2n | P6$_3$mc,P$\bar{6}$2c,P6$_3$mmc |
| | 16L | 73.5 | 26.5 | Hexagonal | 7.542 | - | 65.57 | - | hhℓ:ℓ=2n | " " " |
| | 11L | 71.43 | 28.57 | Hexagonal | 7.54 | - | 43.512 | - | hkℓ:-h+k+ℓ=3n | R3,R$\bar{3}$,R32,R3m,R$\bar{3}$m |
| | 1:2 | 66.67 | 33.33 | Hexagonal | 6.283 | - | 36.878 | - | hkℓ:-h+k+ℓ=3n | " " " " " |
| | TTB | 66 | 34 | Tetragonal | 12.569 | - | 3.957 | - | h0ℓ:h=2n | Pmam,P2$_1$am,Pma2 |
| | 3L* | 75 | 25 | Hexagonal | 9.051 | - | 12.284 | - | h0ℓ:ℓ=2n | P6$_3$cm, P$\bar{6}$c2,P6$_3$mcm |
| | H-1:3* | 75 | 25 | Monoclinic | 14.614 | 3.774 | 6.557 | 98°30' | none | P2,Pm,P2/m |

*Metastable phase obtained from quenched liquid.

composition of this structure was labeled $A_6B_{15.6}O_{42}$ or 27.78 per cent alkali rather than 25 per cent alkali. Ternary compounds isostructural with this phase were reported by Groult et al. [11], with the ideal formula $A_3M_8O_{21}$ or 27.27 per cent alkali.

Specimens of the hexagonal niobates and tantalates from the $Rb_2O$ and $K_2O$ systems were given to Dr. Gatehouse of Monash University for single crystal x-ray diffraction structure determination [10] and to Dr. Yagi at Arizona State University for study by the ultra high resolution electron microscope lattice image technique [12]. Both of these studies indicate that the "9-L", "16-L", and "11-L" designations are misnomers. The designations "9-L", "11-L", and "16-L" should be dropped and a new nomenclature substituted. It is apparent that the "9-L" and "11-L" structures are made up of double hexagonal units of the type described by Gatehouse alternating with isolated octahedra and mirror (twinned) images of the two layers of the pyrochlorestructure. The 16-L structure is an ordered intermediate between the other two phases.

Complete details of the lattice image and structure determinations will be published elsewhere, however, the basic principles are described here. The pyrochlore structure can be written as AaBbCcAaBbCc . . . where A, B, and C are the hexagonal bronze layers and a, b, c are the isolated octahedra. The structure of the "9-L" phase was described by Yagi [12] from the lattice image pictures as:

$$AaBB'a'A' \qquad B'a'A'AaB \qquad Aa\text{-----}$$

where the prime symbol denotes a mirror image (combined with translation or rotation). This can be described as a double block structure and has hexagonal symmetry. The "11-L" structure is:

$$AaBbC \qquad BbCcA \qquad CcAaB \qquad Aa\text{-----}$$

and can be described as a triple block structure with rhombohedral symmetry. Note that in the double block structure ("9-L") each block contains two mirrored "twins" whereas no such mirror "twins" exist in the triple block ("11-L") structure. The ideal basic "9-L" block is:

$$(Aa+B) + (B'a') + 1/2A' = (6+4) + (6) + (2) = 18 \text{ Å}$$

where the basic "11-L" block is:

$$(Aa) + (Bb) + 1/2C = (6) + (6) + (2) = 14 \text{ Å}$$

The "16-L" phase is an ordered intermediate which is hexagonal and contains two of each type of block. It is therefore a four block phase and has the structure:

$$AaBbC \quad BbCC'B'B' \quad C'b'B'a'A' \quad B'a'A'Aab$$

or

"11-L" + "9-L" + "11-L" + "9-L"

or

$$2(18+14) = 2(32) = 64\text{Å}.$$

## 4. Conclusion

Several different structure types were found to be present in the two subsystems examined. The hexagonal bronze stacking sequence similar to that found in the $K_2O$-$Ta_2O_5$ system was found to be present as well as the Gatehouse bronze found in the $K_2O$-$Nb_2O_5$ system. Ion exchange reactions proved that suitable structure types could be easily $K^+$ ion exchanged but $Na^+$ ion exchange lead to excessive volume change and destruction of both ceramic specimens and single crystals. Melt and flux growth yielded single crystals of the HTB, GTB, and the triple block rhombohedral phase in the $Rb_2O$-$Nb_2O_5$ system. In the $Rb_2O$-$Ta_2O_5$ system, single crystals of the large double block hexagonal phase were grown by the flux evaporation method.

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It should be emphasized that the explanation of the crystal chemistry of these phases is due to the cooperation between three separate and distinct groups. This laboratory contributed the syntheses, phase equilibria, unit cell dimensions, and alkali metal oxide ratio. Dr. Gatehouse and his group at Monash University, Clayton, Australia contributed the first solution to the crystal structures and the crystal structure refinements, while Dr. Yagi of the Tokyo Institute of Technology, while a guestworker at Arizona State University, contributed the lattice image studies and their final interpretations as hexagonal bronze-pyrochlore mixtures.

We would like to also give credit to Dr. S. Andersson of Lund Institute of Technology, Sweden, and to Dr. J. Galy of CNRS, Toulous, France for first pointing out the possibility of this hexagonal bronze-pyrochlore stacking sequence.

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